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THE APPLICATION OF CARBONYLATION

AND RELATED REACTIONS TO FATTY

ACID DERIVATIVES

by

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(Trevelyan College)

A thesis submitted to the University of Durham for the

degree of Doctor of Philosophy

Autumn 1987

MEMORANDUM

The work described in this thesis was carried out in the
Department of Chemistry of the University of Durham and at Akzo
Chemie, Littleborough between October 1982 and september 1985. It
has not been submitted for any other degree and is the original
work of the author, except where acknowledged by reference.

ACKNOWLEDGEMENTS

ABSTRACT

The work detailed in this thesis is mainly concerned with the carbonylation of fatty acid derivatives, using carbon monoxide atmospheres in the presence of a transition metal. The two systems under study were the conversion of oleonitrile to a cyano-ester using a cobalt catalyst, and formation of isocyanates from amines in the presence of a palladium salt.

The objectives of each study were: (i) to assess the influence of physical conditions on the reaction (i.e. pressure, time and temperature); (ii) to examine the effect of various additives on the system (i.e. phosphines, iodides and bases); and (iii) to identify any catalytic species observed under reaction conditions. Three major techniques were employed in each study: autoclave reactions, high pressure infra-red studies and atmospheric pressure nitrogen-line chemistry.

The proposed underlying reaction mechanism was examined critically for each system, comparisons being drawn between the postulated catalytic species and those actually observed by high pressure infra-red spectroscopy. The chemical properties of the proposed catalytic intermediates are discussed in relation to the effect of co-reactants on the system.

In the case of the carbonylation of oleonitrile the high pressure infra-red studies are consistent with the proposed reaction mechanism based upon the acyl complex $RCOCo(CO)_4$. Although the infra-red study on the carbonylation of amines did not reveal any definite information, the results of other experiments were found to be consistent with a system based upon a carboxamido species $L_2Pd(Cl)(CONRR')$.

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CHAPTER 1: Introduction to the alkoxycarbonylation of olefins

CHAPTER 2: Experimental

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ABBREVIATIONS

Ph = C_6H_5

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

R = Alkyl

Me = Methyl

Et = Ethyl

THF = Tetrahydrofuran

CHAPTER ONE

INTRODUCTION TO THE ALKOXYCARBONYLATION

OF OLEFINS

1.1. Background Information

The past few decades have seen an enormous growth in the application of new catalytic reactions, both heterogeneous and homogeneous, to industrial processes. The success of these processes is based on their use of cheaper raw materials compared with the classical organic routes; many of which may require multi-stage syntheses. In a large number of systems one of the reactants is carbon monoxide, present either in the pure state or as a mixture with hydrogen, for which a cheap and convenient method of production is required. Currently carbon monoxide is extracted from mixtures of carbon monoxide and hydrogen. Two main separation techniques are currently being used to separate the two gases: The first is selective absorption of carbon monoxide using solutions containing copper (I) salts e.g. $CuAlCl_4$, the carbon monoxide being recovered by heating the solution under reduced pressure. This process generates carbon monoxide with the main impurities being carbon dioxide, nitrogen and methane. The second method for producing carbon monoxide is by low temperature fractional distillation of carbon monoxide/hydrogen mixtures, followed by liquid methane washing. The major impurities in this process are methane and hydrogen.

Mixtures of carbon monoxide and hydrogen are known as synthesis gas, and may be conveniently prepared from many carbonaceous materials, such as coal or petroleum fractions. These materials are combusted in the presence of air or oxygen and/or steam, the crude mixture is the purified to remove soot

and sulphur containing impurities. The gas mixture from this stage has a carbon monoxide to hydrogen ratio dependent upon the starting material and the conditions used. Synthesis gas mixtures with predetermined carbon monoxide to hydrogen ratios can be made by adjustment via the water gas shift reaction, followed by carbon dioxide removal.

i.e. $$CO + H_2O \longrightarrow CO_2 + H_2$$
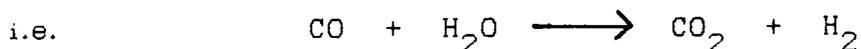
Industrially the majority of catalytic processes employ heterogeneous catalysts for both continuous and batch reactions. One main reason for this is the difficulties involved in the recovery of homogeneous catalysts from the reaction media. The only exceptions to this are processes in which all the reactants and products are volatile, and hence can be easily separated from the catalyst mixture. Homogeneous catalysts however are usually more selective than their heterogeneous counterparts, and hence may find increasing use in industrial processes where the formation of by-products is a serious disadvantage.

Carbonylation reactions are of considerable importance in industrial synthetic organic chemistry, for example in the conversion of methanol to ethanoic acid using a rhodium catalyst. The term carbonylation can be applied to any reaction in which the end product contains a carbonyl group derived form carbon monoxide. Industrially the most widely employed carbonylation reaction is hydroformylation of alkenes to aldehydes, current production being about 5 million tons annually worldwide.

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The term fatty acid can be applied to carboxylic acids with long aliphatic chains. The chain may contain various degrees of unsaturation from to none to greater than three double bonds. These acids are found naturally as the glyceride eters. The free acids are made by hydrolysis of these glycerides followed by acidification. The glycerides are found in the extracts of many plants and animal fats, such as rape seed oil, tallow, and cocoa bean extract. The fatty acids can be converted into many derivatives, common derivatives being amides, nitriles and amines. All of these compounds find industrial uses as, for example, surfactants and lubricants for plastics.

1.2. Carbonylation of alkenes

The reaction studied here is the alkoxycarbonylation of alkenes using a catalyst based upon dicobalt octacarbonyl under high pressures of carbon monoxide and high temperatures (typically 150 - 200 atm, 150 - 200°C). The reaction is one of a general class of reactions which involve the addition of an organic molecule, with an active hydrogen atom to an alkene group with the final product containing a carbonyl group derived from carbon monoxide:-

$$CH_2 = CH_2 \ + \ CO \ + \ ZH \longrightarrow \begin{array}{c} CH_2-CH_2 \\ | \quad\quad | \\ CO \quad H \\ | \\ Z \end{array}$$

ZH = ROH, RNH$_2$, R$_2$NH, RCOOH and RSH
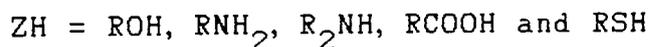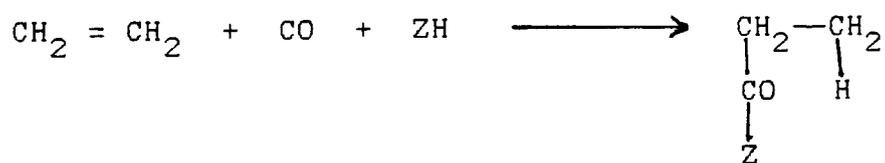
The term alkoxycarbonylation is used when the functional group produced is an ester. When the ZH reagent is water, acids

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are formed and this is known as hydrocarboxylation, although formally this process should be classified as hydroxy-carbonylation. Another class of carbonylation reactions which do not involve the addition of hydrogen but involve the addition of other groups to a double bond instead of hydrogen are shown below:-

$$CH_2 = CH_2 \; + \; CO$$

$$\xrightarrow{\;PdCl_2\;} CH_2ClCH_2COCl$$

$$\xrightarrow{\;CCl_4\;} Cl_3CCH_2CH_2COCl$$

$$\xrightarrow{\;ROH\;} ROOCCH_2CH_2COOR$$

$$\xrightarrow{\;C_2H_5OH\;} C_2H_5OCH_2CH_2COOC_2H_5$$

$$\xrightarrow{\;CH_3COOH\;} CH_3COOCH_2CH_2COOH$$

$$\xrightarrow{\;ROH\;} CH_2 = CHCOOR$$
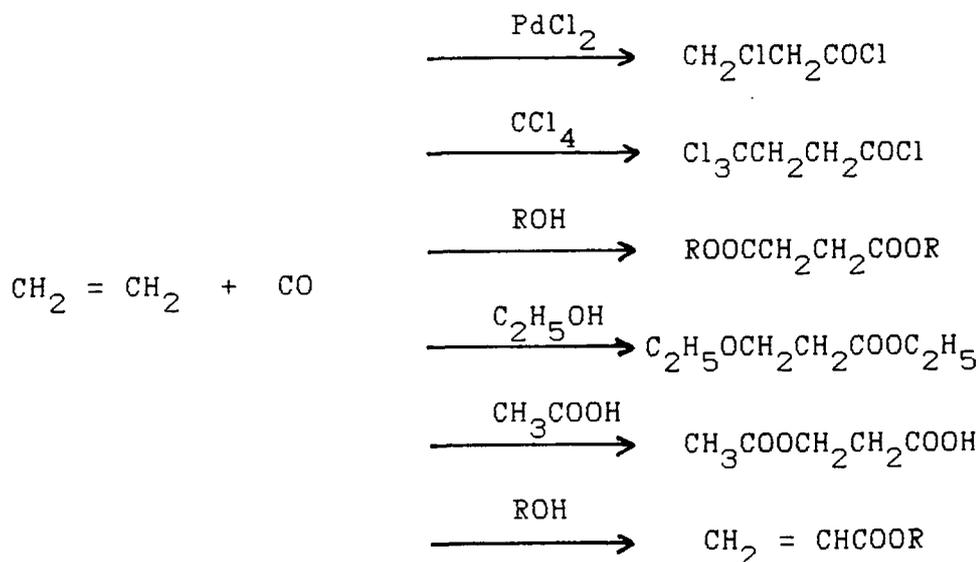
Many of the reactions involve the stoichiometeric use of a transition metal species, commonly of palladium. These reactions are mechanistically somewhat different to the previous examples and will not be discussed further.

The alkoxycarbonylation of alkene substrates is formally analogous to the hydroformylation of alkenes, which involves the addition of a hydrogen and a formyl group to the same substrate type i.e. ZH is equivalent to hydrogen. The first reports of acid and ester synthesis were given by Reppe (1), who reacted nickel tetracarbonyl with acetylene. The reactions however require a stoichiometric quantity of the transition metal. The first reports of catalytic formation of esters were

by Dupont et al (2), and Natta and Pino (3) during their studies of the hydroformylation of α-pinene in methanol, the catalyst used being derived from metallic cobalt.

Stoichiometric synthesis of acids and esters has been widely studied, chiefly using nickel tetracarbonyl as the transition metal species (4). The reaction between alkenes and nickel tetracarbonyl is carried out in the presence of an excess of water and alcohol. The reaction requires the use of elevated temperatures, i.e. 250 - 300°C being typical when no promoters are used in the system. The addition of halide ions, usually hydrogen chloride, or the presence of acids in the reaction media greatly reduces the temperature required for reaction to occur. The reaction also seems to be influenced by ultra-violet light, the yield being enhanced by exposure.

$$Me(CH_2)_5CH=CH_2 \ + \ Ni(CO)_4 \ + \ H_2O \ \xrightarrow[50-60^oC]{HCl} \ Me(CH_2)_5CHCOOH \ + \ NiCl_2$$
$$Me$$
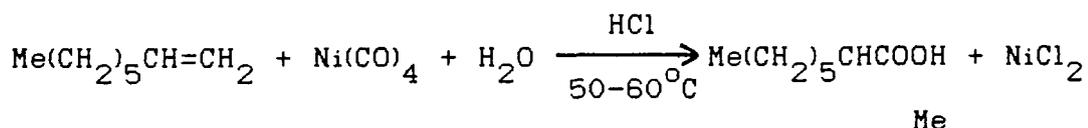
This reaction can also be carried out using alkynes. For example, ethyne will react to give acrylic acid. Iron compounds have also been used in stoichiometric synthesis of acids and esters; these are produced by reaction of alkenes with potassium hydrido tetracarbonyl ferrate. The intermediate acyl metal species, which are presumably formed, are oxidised to esters using iodine in ethanol. Another route not involving alkenes, uses alkyl halides and sodium tetracarbonylferrate, the products being obtained by oxidation of the resulting metal complexes.

In the case of cobalt mediated formation of acids and

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esters, the products are formed by reaction of acyl cobalt species with either an alcohol or an alcohol and iodine. The acyl cobalt tetracarbonyl complexes may be prepared by direct reaction of an olefin with hydrido cobalt tetracarbonyl, or via reaction of an alkyl halide with sodium tetracarbonyl cobaltate. Heck reported the direct alcoholysis of acyl cobalt tetracarbonyl with methanol (5), the proposed cobalt species formed being the hydrido cobalt tetracarbonyl. This species was not detected however, presumably due to its instability at $50^{\circ}C$ without a carbon monoxide atmosphere.

The mechanism proposed for the catalytic hydroxy-carbonylation of alkenes using cobalt based catalysts is believed to be formally similar to the reaction scheme generally accepted for the hydroformylation reaction. The active cobalt complex, proposed as being formed via the water gas shift reaction:-

$$CO + H_2 \longrightarrow CO_2 + H_2$$
$$H_2 + Co_2(CO)_8 \longrightarrow 2HCo(CO)_4$$
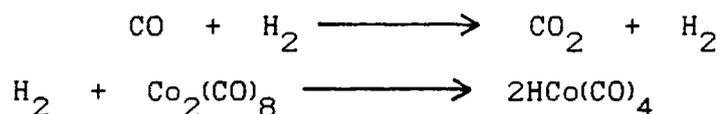
However there is neither direct evidence for the existance of the hydrido species nor for the importance of the water gas shift reaction in alkoxycarbonylation. Kinetic studies of this reaction and the hydroxycarbonylation reaction have shown that these reactions are much slower than the corresponding hydro-formylation reaction (6). The other main differences found were in the order of these reactions with respect to the olefin substrate. In the case of hydroformylation, the order is about 1; this drops to 0.5 for hydroxycarbonylation and is

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approximately zero for the alkoxy-carbonylation reaction.

The addition of nitrogen bases to the alkoxycarbonylation reaction has a dramatic effect on the yields obtained. If strong nitrogen bases such as triethylamine are used then this virtually stops the reaction and only low yields are obtained (7). This may be explained by reaction of the base with the hydrido cobalt complex to give relatively stable salts, thus preventing the addition of the hydrido complex to the alkene. If, however, a milder base such as pyridine is used an increase in yield is obtained (8). This has been explained by postulating that the base aids the alcoholysis of the acyl cobalt complex via formation of a pyridinium species:-

$$RCOCo(CO)_4 \quad + \quad py \quad \longrightarrow \quad RCOpy^+ \quad + \quad Co(CO)_4^-$$
$$RCOpy^+ \quad + \quad R'OH \quad \longrightarrow \quad RCOOR' \quad + \quad H^+ \quad + \quad py$$
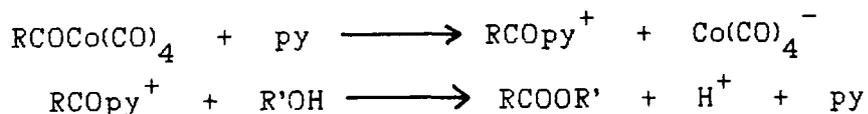
This explanation also relies on the alcoholysis of the acyl cobalt species being the rate determining step in the reaction. Support for this comes from the change in order of the reaction, with respect to the alkene, on the addition of the pyridine from about zero to an order of one (9).

Although no spectroscopic studies have been conducted on the hydroxycarbonylation or alkoxycarbonylation reactions, studies have been carried out on the hydroformylation reaction using cobalt catalysts (10, 11). These studies have revealed the existance of both the hydrido-tetracarbonyl cobalt complex and the acyl-tetracarbonyl cobalt species in the reaction mixture. The studies also show that for terminal alkenes the rate determining step for the hydroformylation reaction is the

hydrogenation of the acyl complex to give the aldehyde.

The study undertaken here is concerned with an examination of some of the intermediates involved in the alkoxycarbonylation reaction. The investigation is concerned with the effect of catalyst type, co-reactants such as halides or pyridine, and physical conditions on the conversion and selectivity of the reaction. The reaction has also been studied by infra-red spectroscopy both at room pressure and under 'in-situ' conditions, to provide an assessment of proposed catalytic intermediates and possible reaction mechanisms.

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CHAPTER TWO

EXPERIMENTAL

2.1 Techniques

2.1.1. Manipulation of air/or moisture sensitive materials

All reactions requiring the absence of air/moisture were carried out under a dry nitrogen atmosphere with all solvents dried by suitable methods and either stored under dry nitrogen or degassed prior to use. The nitrogen was obtained from the general laboratory supply and subsequently dried by passage through concentrated sulphuric acid and phosphorus pentoxide. The dry nitrogen was then connected directly to the vacuum line so that apparatus could be readily evacuated and refilled with an inert atmosphere. The vacuum line was fitted with a mercury diffusion pump and was capable of generation a vacuum exceeding 0.05mm Hg.

Samples which reqiured more complex manipulations (i.e. for infra-red spectroscopy) were handled in a dry nitrogen glove box. The box was supplied with nitrogen dried as above and the atmosphere was continually recycled through a phosphorus pentoxide tower.

2.1.2. Physical techniques

Chromatography

Liquid samples were analysed using gas liquid chromatography (g.l.c.), various column types were selected depending upon the boiling point and chemical functionality of the compounds. The higher boiling materials were analysed using a Varian 3700 series instrument equipped with a 1 meter 3mm o.d. stainless steel column packed with 10% OV-101 on

chromosorb G. The instrument was equipped with a flame

ionisation detector. Details of the temperature programme were

varied depending upon the sample being analysed, but typical

conditions were:-

t = 0 to 5 minutes   – at $170^{O}C$

t = 5 minutes onwards – an increase in temperature of $10^{O}C/min$.

to $280^{O}C$

Injector temperature at $270^{O}C$

Amine analysis was carried out on a Pye Unicam 580B

instrument using a three metre glass column packed with

chromosorb 20M (2% KOH washed).

Hexenes and low boiling materials were analysed using a

Hewlett Packard 5890A instrument equipped with a twenty five

metre SE 30 capillary column. The temperature programme was

typically:-

t = 0 to 5 minutes   – at $30^{O}C$

t = 5 minutes onwards – an increase in temperature at $10^{O}C/min$.

to $170^{O}C$

The composition of the product mixture could be

determined by one of two methods, the first method required the

presence of an internal standard in the initial reaction

mixture which would not react under the conditions employed in

the experiment. A typical internal standard used was n-

hexadecane. From the area ratios before and after reaction, the

amount of reactant in the product mixture could be calculated

thus:-

$$W_i = W_{iO} * (a_i/a_r) / (a_{iO}/a_{rO})$$

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where W_i = weight of i-th component after the experiment

W_{iO} = weight of i-th component before the experiment

a_i/a_r = area ratio for the i-th component to the reference after the experiment

a_{iO}/a_{rO} = area ratio for the i-th component to the reference before the experiment

The second method for calculating the composition of a mixture involves the use of response factors for each component within the mixture. These directly relate the area of a peak to the weight percentage through the following expression:-

$$\%W_i = \frac{f_i * a_i}{\Sigma f_i * a_i} * 100$$

where W_i = weight percent of i-th component

a_i = area of i-th component

f_i = response factor for i-th component

Each weight percentage can then be normalised such that the total number of moles of compounds derived from a given reactant equals the number of moles of compound initially charged. These results, for both methods, can then be used to calculate the percentage molar conversion and molar selectivity via the following equations:-

% molar conversion = $\frac{\text{number of moles converted}}{\text{number of moles charged}} * 100$

% molar selectivity = $\frac{\text{number of moles of that product}}{\text{number of moles reactant consumed}} * 100$

In the case of compounds very similar in nature, or for a series of isomers, the response factors are the same and hence

direct area ratios can be used.

^{1}H and ^{13}C n.m.r. spectroscopy

Routine ^{1}H analysis of samples was accomplished using a 60 MHz Varian spectrometer. High resolution ^{1}H and ^{13}C spectra were recorded on either a Bruker W H 360 or a Bruker W M 300 W B courtesy of Newcastle and Edinburgh Universities repectively.

Mass spectroscopy

Mass spectra were recorded using a V.G. 7070E instrument, ionisation being achieved either with a 70 eV electron beam or by using isobutane as a chemical ionising gas. Sample insertion was via either a direct insertion probe or via a linked g.l.c. machine.

Infra-red spectroscopy

Routine infra-red (4000 - 250 cm^{-1}) were recorded on a Perkin Elmer 577 or 457 grating spectrometer. Solid samples were prepared as nujol mulls, in an inert atmosphere for air/moisture sensitive samples, or as KBr discs for samples of air/moisture stable material. Solution spectra were recorded using a 0.1mm solution cell with either KBr or CaF$_2$ windows.

High pressure solution spectra were recorded on a Perkin Elmer 257 spectrometer, modified to accept the high pressure solution cells by the use of four extra concave mirrors. The system is similar to that used by Whyman (1), except that an extra cell is used in the reference beam to compensate for solvent and dissolved gas absorptions. The cells are based off a design by I.C.I. and use CaF$_2$ windows. These were found to

extrude slowly during reaction (2) thus changing the path length. Spectra were recorded in the region 2300 cm^{-1} to 1400 cm^{-1}. A cross section of the cell is shown in Figure 2.1.

2.1.3. Analytical methods

Carbon, hydrogen and nitrogen

Carbon, hydrogen and nitrogen analyses were determined by microcombustion using a Perkin Elmer 240 elemental analyser.

Metals

Metals were determined by atomic absorption spectrophotometry using a Perkin Elmer 403 instrument.

Phosphorus and halogens

Phosphorus and chlorine analyses were determined by initial treatment of a weighed sample with oxygen in a nickel Parr bomb. The residue is acidified with concentrated nitric acid and diluted to 100ml with distilled water. Phosphorus is measured by treatment of a suitable portion of the solution with ammonium molybdate/ammonium vanadate and the measurement of the absorbance at 420 μm using a Pye Unicam SP 500 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 iodometerically following a Schoniger oxygen flask combustion.

2.2. Preparation and purification of starting materials

2.2.1. Solvents

Methanol :- was purified by reacting Analar methanol with magnesium turnings (1g per 100ml) under a dry nitrogen
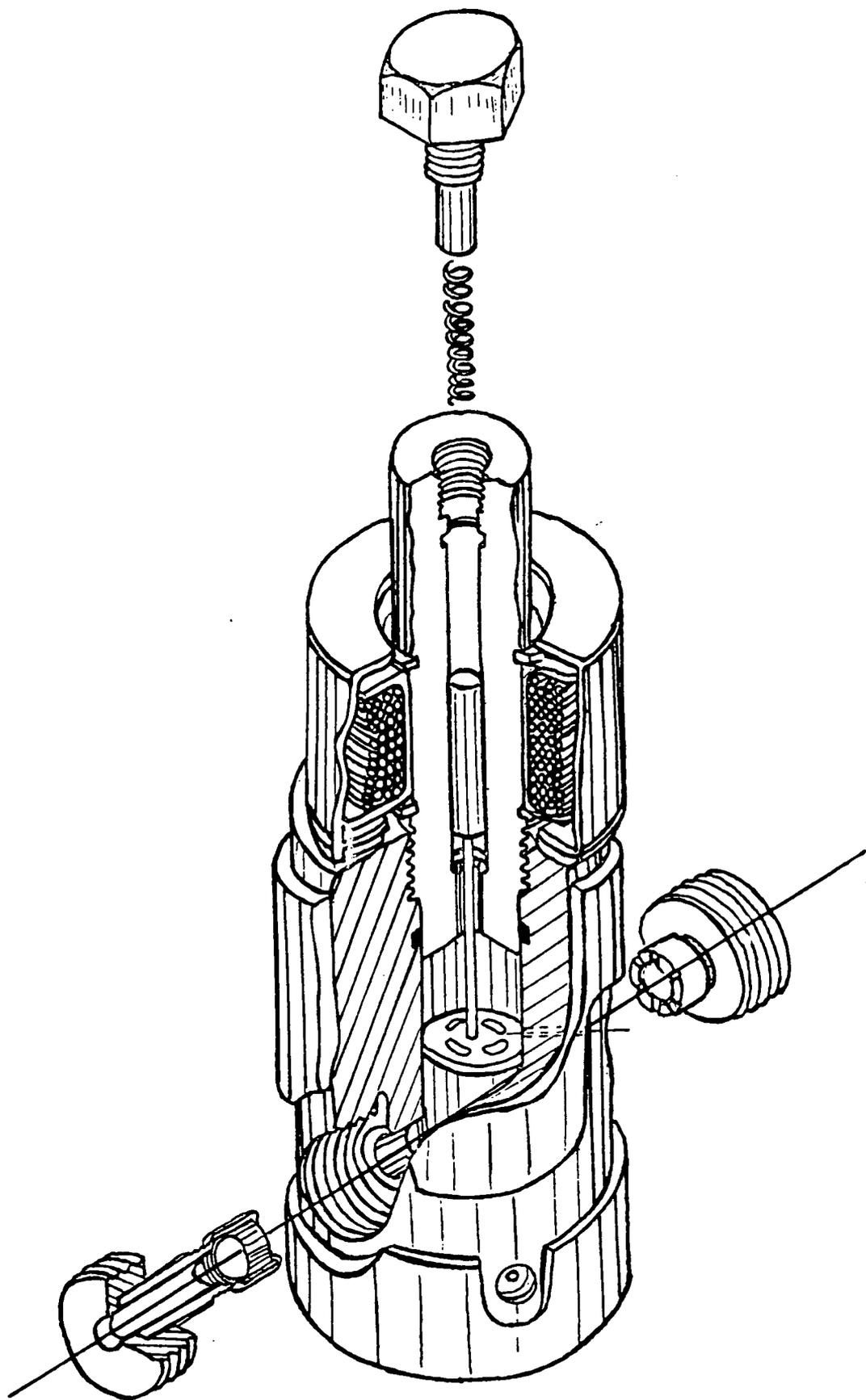
Figure 2.1. High pressure infra-red cell

atmosphere. After the reaction had ceased the methanol was distilled onto 3A molecular sieve and stored under a dry atmosphere.

THF :- was dried by refluxing over potassium metal followed by distillation under a dry nitrogen blanket.

Petroleum ethers, hexane and toluene :- were either used as obtained or dried prior to use by storing over sodium wire. All other solvents were used without purification.

2.2.2. Gasses

The gasses use in he high pressure experiments were supplied as follows:- nitrogen and hydrogen from British Oxygen Company, and carbon monoxide (C.P. grade) by Air Products; all gasses were used directly without further purification.

2.2.3. Starting materials

Dicobalt octacarbonyl and PPNCo(CO)$_4$ were obtained from Strem Chemicals and were used without purification. Phosphine ligands were supplied by British Drug House and used as bought. Organonitrile species from British Drug House were stored over 3A molecular sieve prior to use. Oleonitrile was provided by Akzo Chemie, the crude material being distilled under high vacuum (c.a. 0.01mm Hg). Th fraction at b.p. 155 - 165°C was collected and stored over 3A molecular sieve. Fatty acid amines, except di-octadecylamine which was obtained from Fluka, were generously supplied by Akzo Chemie and used without further purification. Palladium (II) chloride and palladium (II) acetate were obtained from Aldrich. All other materials were of the best commercially obtainable grades and were used

as supplied without purification unless specified.

2.3. High pressure equipment

The high pressure work detailed in this thesis was carried out using three different autoclave designs. The infra-red studies were accomplished using an autoclave design similar to that used by Whyman (1). The autoclave was made from a titanium alloy and was capable of operating up to 350 Bar 250°C. (See Figure 2.1.). The second design was made by Rockhurst Engineers; made from 316 stainless steel capable of operating at 300 Bar and 200°C. The autoclave had a 150 cm^3 capacity and was equipped with a Magna drive (see Figure 2.2.). The third design employed used for some of the N-chloroamine work together with the Rockhurst design, were 300ml and 600ml Parr autoclaves.

Pressure measurements were made using a Wikka pressure transducer operating in the range 0 to 50 Bar, the output from the transducer being recorded on an X-Y plotter for gas uptake studies.

All high pressure reactions were carried out in purpose built high pressure facility. This consisted of a high pressure cubicle and separate control room, the walls of the high pressure cubicle being constructed from steel reinforced concrete. All manipulations, as regards temperature and pressure, of the autoclaves were accomplished remotely via closed circuit T.V., until the system had been depressurised after cooling.

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Figure 2.2. 150cm^3 Rockhurst autoclave

MAGNADRIVE II

TO SAMPLE VALVES

GAS INLET

VITON 'O' RINGS
PTFE

SAMPLE TUBE

THERMOCOUPLE WELL

PADDLE

316 STAINLESS STEEL
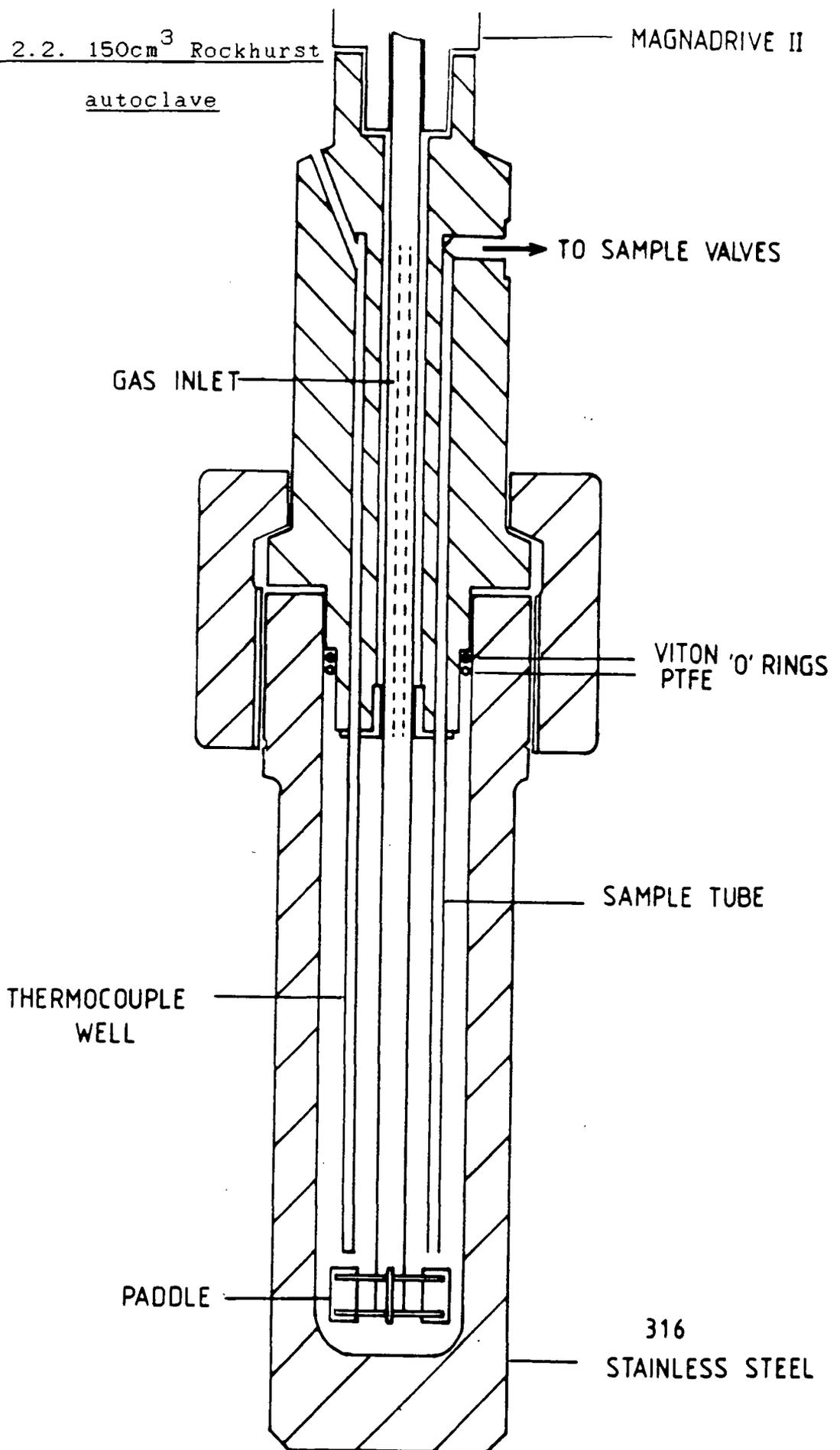
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CHAPTER THREE

OLEONITRILE/COBALT/METHANOL

SYSTEM

3.1. Introduction

The work detailed in this chapter is concerned with (i) the reaction between dicobalt octacarbonyl and Lewis bases, such as methanol and organo-nitrile compounds, studied at atmospheric pressure and (ii) a systematic study of the high pressure alkoxycarbonylation reaction of oleonitrile. The main aim of this chapter is to report the effect of temperature, pressure, catalyst form and addition of co-reactants on the latter reaction.

3.2. Low pressure study of the dicobalt octacarbonyl/Lewis base reaction

3.2.1. Experimental

(a) Methanol and dicobalt octacarbonyl at room temperature

When red/brown crystals of dicobalt octacarbonyl (0.3g, 1 mmol) were added to dry methanol under an inert dry nitrogen atmosphere, a dark red/brown solution was initially formed. This colour persists for some time, gradually fading until the solution, after 2.5 to 3 hours, has a pale pink appearance. During this period a rapid evolution of gas was initially observed, the rate decreasing as the reaction proceeded. The solution remains unchanged as long as no oxygen is admitted into the system. Air causes the solution to loose its pinkness and a purple solid to be deposited, this solid gave no infra-red spectra in the carbonyl stretching frequency region and is presumably cobalt oxide.

During the reaction samples were taken at various times and the infra-red spectra, in the region $2200 - 1600$ cm^{-1},

recorded. On addition of the dicobalt octacarbonyl the solution

showed peaks at 2070(m), 2040(m) and 1905(s) cm^{-1}. The peak at

2070(m) cm^{-1} was found to weaken quickly during the first ten

minutes. The remaining peaks were present throughout the

experiment, only the peak at 1905(vs) cm^{-1} disappearing on

exposure of the solution to air. The peaks observed were

assigned as follows :- 2040(m) cm^{-1} is due to the methanol and

could obscure other carbonyl species which may absorb in this

region. The other peak at 1905(s) cm^{-1} is due to the tetrahedral

$Co(CO)_4^-$ ion. The initial peak at 2070(m) cm^{-1} was due to a

terminal carbonyl stretching frequency band of dissolved

molecular dicobalt octacarbonyl.

(b) Methanol and dicobalt octacarbonyl at 50^oC

The above reaction was repeated at a constant temperature

of 50^oC. On the addition of the dicobalt octacarbonyl the same

red/brown solution was initially formed but was found to fade to

the pink solution more quickly. The infra-red spectra showed the

same peaks as before, only the 2070(m) cm^{-1} peak decreasing in

intensity far more rapidly. After heating for several hours the

solution lost its pink colour and a dark grey precipitate

formed; this process was accompanied by a reduction in the

intensity of the 1905 cm^{-1} peak which finally disappeared.

(c) Acetonitrile and dicobalt octacarbonyl at room

temperature.

The reaction between acetonitrile (30ml) and dicobalt

octacarbonyl (0.3g, 1 mmol) was similar to the reaction with

methanol. The initial peak at 2070 cm^{-1} due to dissolved

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molecular dicobalt octacarbonyl was less prominent in the initial period. When the system was heated to reflux the 1890(s) cm^{-1} peak due to the $Co(CO)_4^-$ ion slowly decreased in intensity until finally no carbonyl stretching frequency bands were observed and a fine dark grey precipitate of cobalt metal was formed.

(d) Benzylnitrile and dicobalt octacarbonyl.

Addition of benzylnitrile (30ml) to dicobalt octacarbonyl (0.3g, 1mmol) produced the same dark red/brown solution as above. However the evolution of gas was noted to be significantly slower. This dark red/brown colour persisted for several days, only gradually fading, but the solution did not turn the final pink colour as in the above cases. On heating to 50^oC for several hours the solution finally turned pink, further heating caused decomposition of the cobalt carbonyl species present, namely $Co(CO)_4^-$, to give cobalt metal. In studies of this reaction peaks were initially present at 2070(m), 2040(s), 2020(m,sh) and 1890(vs) cm^{-1}. These peaks persisted for several hours, the peaks at 2070 and 2040 cm^{-1} gradually weakening. During this time two new peaks appeared at 2000 and 1985 cm which gradually increased in intensity with time. On heating to 110^oC all the carbonyl peaks except to 1895(vs) cm^{-1} peak, disappeared; with continued heating this peak also decreased in intensity until finally no peaks were observed in the carbonyl stretching frequency region.

(e) Oleonitrile, propanonirtile and butanonitrile with dicobalt octacarbonyl.

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The above reactions were investigated with the afore mentioned organonitrile compounds. Their behaviour was similar to the case above with benzylnitrile, only the reaction rates differing slightly. The infra-red peaks observed were within 5 cm^{-1} of the peaks reported above in the reaction with benzyl-nitrile. In all cases attempted isolation of any carbonyl species was found difficult due to the high boiling nature of the organic nitriles and led to the decomposition of these metal species to give cobalt metal. Examples of methods used were; (i) removal of the organic liquids by pumping under vacuum, and (ii) addition of another solvent to precipitate insoluble materials.

(f) Reaction of an organo-nitrile with dicobalt octacarbonyl in the presence of methanol.

A solution of an organo-nitrile e.g. oleonitrile (10ml), in methanol (30ml) was added to dicobalt octacarbonyl (0.3g, 1mmol). The experiment followed the same course as in the initial reaction between methanol and dicobalt octacarbonyl with none of the new carbonyl absorptions at 2000 and 1985 cm^{-1} appearing.

3.2.2. <u>Discussion</u>

The reaction between a Lewis base and dicobalt octa-carbonyl is fairly complex depending upon the nature of the base used. In the case of strong Lewis bases, such as methanol, the dicobalt octacarbonyl dissolves in the molecular form initially, as indicated by the presence of the terminal carbonyl stretching frequency bands for $Co_2(CO)_8$ (1) at 2075 cm^{-1}. There then follows a fairly rapid reaction to form $Co(CO)_4^-$ and $Co(MeOH)_6^{2+}$

(2), the cobalt (II) ion giving the characteristic pink colour
to the solution. This solution is only stable in the absence of
oxygen and at ambient temperatures or lower. If the pink
solution is heated or if the initial reaction between methanol
and dicobalt octacarbonyl is carried out at $50^{o}C$, the pink
colouration of the solution rapidly fades and a dark grey
precipitate of cobalt metal is deposited. In the case of
acetonitrile the same qualitative results are obtained only the
time scale is different. The disproportionation reaction is
generally applicable to a wide variety of oxygen or nitrogen
containing strong Lewis bases (3) to give cobalt (II)/cobalt
(-1) complexes as follows:-

$$3Co_2(CO)_8 + 2nB \longrightarrow 2CoB_n^{2+} + 4Co(CO)_4^- + 8CO$$
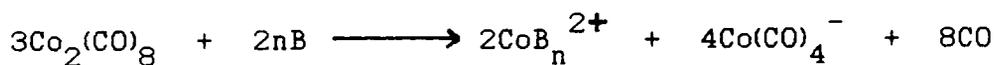
The value of n is usually six for unidentate ligands such as
methanol or acetonitrile and three for bidentate ligands.

In the case of longer chain nitrile species the reaction is not
as straight forward; a similar result was found by Wender (2)
in the reaction of butanol with dicobalt octacarbonyl, which did
not produce the $Co(CO)_4^-$ ion the product was claimed to to be
$Co_2(CO)_5(Base)$. This suggests a different reaction pathway,
possibly similar to the reaction mechanism proposed by
Stanghellini et al (4) in their study of the reaction of
dicobalt octacarbonyl with various amine ligands:-

$$Co_2(CO)_8$$

$$Co_2(CO)_8L \quad\quad\quad Co_2(CO)_7$$

$$Co_2(CO)_8L_2 \quad\quad\quad Co_2(CO)_7L$$

$$Co_2(CO)_7L_3 \quad\quad\quad Co_2(CO)_7L_2$$
$$\text{L} \quad \text{-CO} \quad\quad\quad \text{-CO}$$

$$\downarrow \text{-CO}$$

$$[Co(CO)_2L_3][Co(CO)_4] \quad\quad\quad [Co(CO)_3L_2][Co(CO)_4]$$
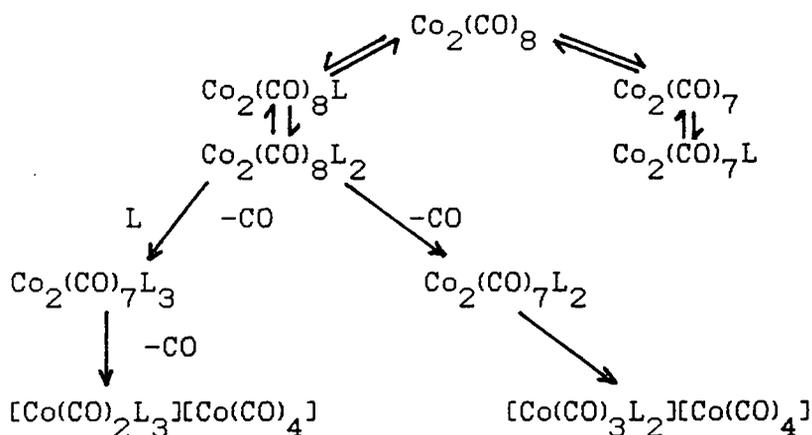
The existance of many of the above species has not been
proven, with some of these complexes being greater than 18
electron species. Thus these may only exist as transition
states, if at all, as they represent complexes with more ligands
than is necessary to give co-ordinatively saturated species.

In the case of the longer chain organo-nitrile species the
bulk of these ligands may prevent the substitution reaction
proceeding as far as the $CoL_6[Co(CO)_4]_2$ complex. Also the
bonding nature of the nitrile group is such that it is only a
weak π-acceptor and a moderate σ-donating ligand compared with
the stronger σ-donating alcohols, they are thus poorer ligands.
The existance of some of the partially substituted complexes
above could explain the unassigned peaks in the infra-red but
cannot be definitely ascribed to such species. When methanol is
added it displaces the larger nitrile ligands and hence produces
the characteristic cobalt (II)/cobalt (-1) complex. The
formation of cobalt (-1) species are not in agreement with
earlier theories (5), which postulated the loss of one or more
carbonyl groups and the substitution by a base to give a neutral
di-nuclear cobalt complex:-

i.e. $Co_2(CO)_8$ + B $\longrightarrow\!\!\!\!\times\!\!\!\!\longrightarrow$ $Co_2(CO)_5B$ + 3CO
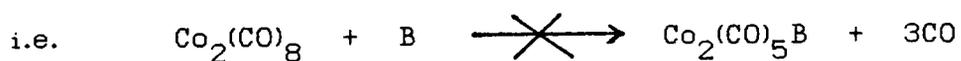
In the reaction between methanol and dicobalt octacarbonyl intermediate formation of the species $[Co(CO)_4B]^+$ was postulated (2). Evidence for the existance of such a species was reported by Tucci et al (6). Their study involved the reaction of dicobalt octacarbonyl with an alcohol or water in the presence of an ion-exchange resin, and showed that the complex cation was only stable below 0°C. These cations are also only observed in the free state with strong Lewis bases such as piperidine (3). The final product is reported to be $[C_5H_{10}NHCo(CO)_4^+][Co(CO)_4^-]$.
The $Co(CO)_4^-$ ion generated in these Lewis base solutions is only weakly basic due to the large acidity of $HCo(CO)_4$. However $Co(CO)_4^-$ is reported to be a comparable nucleophile to the methoxide ion. The α-protons of organo-nitrile compounds are rendered more acidic due to the electron withdrawing effect of the cyano group. Also the carbanion formed by removal of one of these protons can be stabilised via conjugation with the π-system of the cyano group. Analysis of the nitrile solution for carbanion derived materials indicated that no reaction between $Co(CO)_4^-$ and the nitrile had occurred even when the solutions were refluxed at 100°C for several hours.

If generated, an anionic nitrile species would undergo further reaction to produce a variety of organic species. The main reaction pathway would involve nucleophilic attack by the anionic species on further nitrile functionalities:-

i.e.

$$X- \;+\; RCH_2CN \longrightarrow RCH_2C\underset{X}{\overset{N-}{=}}$$

$$XH \;+\; \overset{-}{RCHCN} \longleftrightarrow RCH=C=N-$$

$$RCH_2C\equiv N \overset{}{\underset{\overline{RCHCN}}{\curvearrowright}} \longrightarrow \underset{RCHCN}{RCH_2C=N-}$$

$$RCH_2C\overset{N-}{\underset{X}{\diagup}} \longrightarrow \underset{CH_2R}{C\equiv N} \longrightarrow \underset{X \quad CH_2R}{RCH_2C=N-C=N-}$$
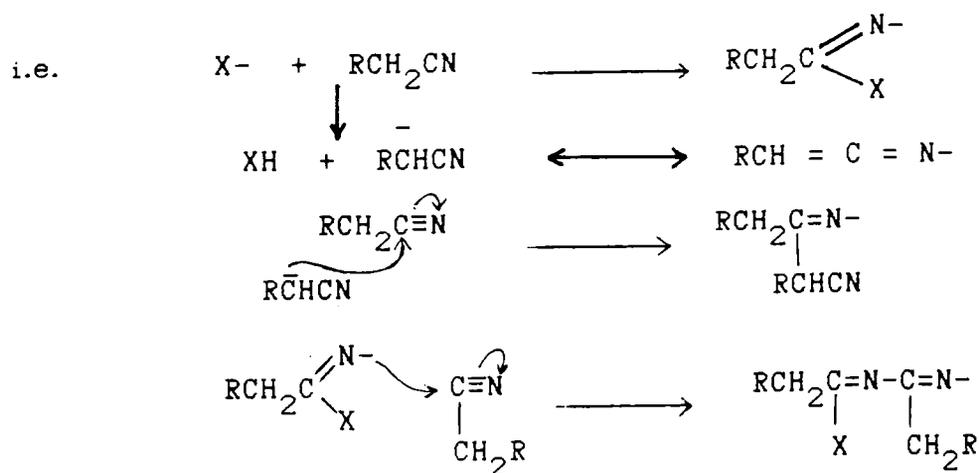
By repeating this last step polymeric materials can be formed.

If however, X = RCHCN then cyclisation could occur at this stage to give a pyrimidine on hydrolysis:-

$$\text{(pyrimidine reaction scheme)} \quad -H_3O^+ \rightarrow$$
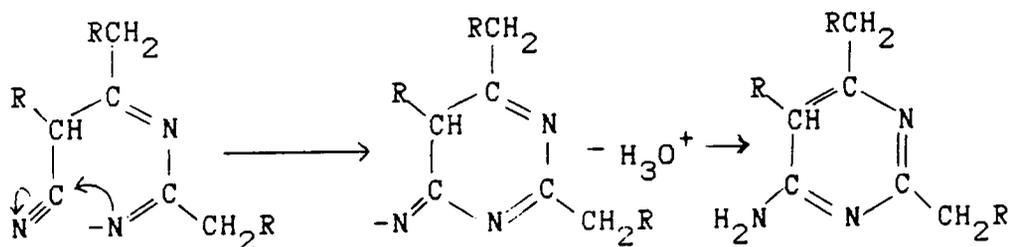
in the case of X = Co(CO)$_4^-$ triazines could result by a similar process:-

$$\text{(triazine reaction scheme)} \quad + \quad Co(CO)_4^-$$
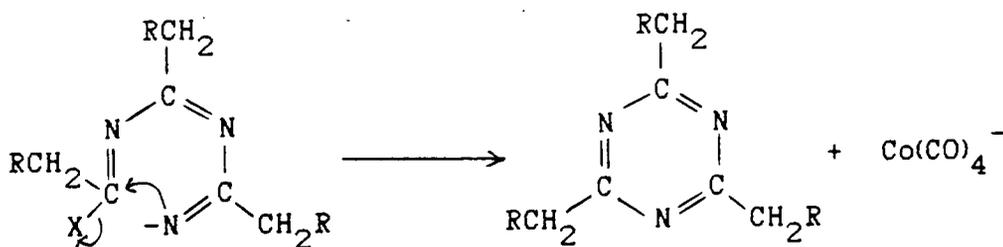
3.3. Formation of MeCo(CO)$_4$ in the presence of Lewis bases

Aim:- to generate MeCo(CO)$_4$ and MeCOCo(CO)$_4$ in the presence of Lewis bases and to study possible interactions with oleonitrile.

3.3.1. Experimental

(a) Reaction of Co(CO)$_4^-$ with methyl iodide in acetonitrile.

Acetonitrile (30ml) was allowed to react with dicobalt

octacarbonyl (0.3g, 1 mmol) for two hours under an inert atmosphere. Methyl iodide (0.3g, 2 mmol) when added to the pink solution caused the solution to quickly turn a green colour which persisted throughout the rest of the experiment. The excess acetonitrile when removed under vacuum, left a green solid which when analysed gave a Co to I ratio of 1:0.76. The solid was extracted with acetonitrile then filtered to give a grey powder and a green solution. The grey solid showed no distinct infra-red spectrum as expected for cobalt metal. After evaporating off the acetonitrile and pumping to dryness, the green solid gave Co 14.7%, I 64.9%, C 11.7%, H 2.09% and N 5.9% corresponding to $Co(MeCN)_{1.9}I_2$.

Infra-red observation of the carbonyl stretching frequency region initially showed only the $Co(CO)_4^-$ peak at 1895(vs) cm^{-1}. On addition of the methyl iodide this quickly changed and new absorptions appeared at 2105(m), 2055(vs), 2035(vs), 2005(vs), 1955(m), 1935(m) and 1710(m) cm^{-1}. All of these peaks persisted throughout the rest of the experiment except the peaks at 1955 and 1935 cm^{-1} which disappeared after 1 hour. These two peaks could not be assigned to any carbonyl species. However the remaining peaks are consistent with the formation of $MeCOCo(CO)_4$ (peaks reported at 2105(w), 2048(m), 2026(m), 2007(s), 1715(m) cm^{-1} (7)).

   (b) Reaction of $Co(CO)_4^-$ with methyl iodide in the
       presence of oleonitrile.

Oleonitrile (10ml) in dry THF (20 ml) was allowed to react with dicobalt octacarbonyl (0.3g, 1 mmol) for several

hours; methyl iodide (0.3g, 2 mmol) was then added. The reaction proceeded as described above, with an extra peak in the infra-red due to THF at 1990 cm^{-1}. The infra-red bands due to the $MeCOCo(CO)_4$ species were present in the reaction mixture for several days. The reaction was also repeated at $-20^{\circ}C$ by cooling the initial oleonitrile/dicobalt octacarbonyl solution after several hours at ambient temperature, followed by the addition of the methyl iodide. No new absorptions were found in the infra-red and no reaction between $MeCOCo(CO)_4$ and oleonitrile was found on analysis of the reaction mixture. Other nitrile species were used in similar reactions and gave qualitatively the same results. If methyl iodide was replaced by iodoethane then the reaction was observed to proceed far more slowly, the $Co(CO)_4$ ion carbonyl stretching frequency band was present for several hours after the addition of the iodoethane.

3.3.2. Discussion

The anion $Co(CO)_4^-$ is quite nucleophilic (8) towards methyl iodide to form, rapidly, the methyl cobalt tetracarbonyl complex. This complex is unstable above $-35^{\circ}C$ and is quickly converted, first via the acyl tricarbonyl species, to the acyl cobalt tetracarbonyl complex, through carbon monoxide insertion and absorption (9):-

$$MeCo(CO)_4 \rightleftharpoons MeCOCo(CO)_3 \rightleftharpoons MeCOCo(CO)_4$$
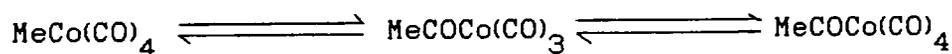
As can be seen, the product has an extra carbon monoxide molecule and hence some other cobalt species must decompose to supply the extra carbonyl group.

The alkyl and acyl cobalt tetracarbonyl are unstable

unless the alkyl or acyl group is perfluorinated. Reaction of a $Co(CO)_4^-$ salt with an acyl halide provides a general method of synthesis of these species (10). The stability of the perfluoro-species has been attributed to the electron with-drawing effect of these perfluoro alkyl groups. In the case of $MeCOCo(CO)_4$ it starts to decompose in the pure state at $-20^{\circ}C$ and can undergo decarbonylation to $MeCo(CO)_4$ at lower temperatures and subsequently decomposition above $-35^{\circ}C$ (11). The solution behaviour of these species is, however, quite different and a dilute solution of $MeCOCo(CO)_4$ is relatively stable at room temperature particularly in the presence of a carbon monoxide atmosphere. The reaction of alkyl cobalt tetracarbonyl to form the acyl species is believed to be a rapid equilibrium with the predominant species being the acyl complex. The existance of a peak at 1720 cm^{-1} in the infra-red of the alkyl species has been postulated as evidence for the existance of acyl tricarbonyl species; however a better explanation is the formation of either some $RCOCo(CO)_4$ or ketones via decomposition.

Organo-nitrile compounds are known to react with organometallic reagents. There are two main reaction pathways observed:-

$$RC{\equiv}N \; + \; MR' \longrightarrow R{-}C \overset{R'}{=} N - M$$

$$\underset{\underset{N:}{\overset{\displaystyle C}{\|\|}}}{\overset{\overset{\displaystyle H}{\nearrow}}{RCH}} \;\; \underset{\overset{\displaystyle M}{\nearrow}}{\overset{\displaystyle R'}{\underset{|}{\big(}}} \longrightarrow RCHCN \; + \; M^+ \; + \; R'H$$
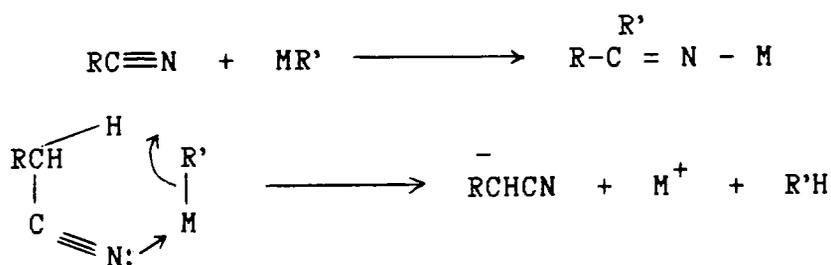
Both reaction pathways are observed with Grignard reagents. The

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anions formed can undergo further reaction to give dimers, trimers and substituted pyrimidines as mentioned earlier. However none of these products were noted in any of the nitriles studied above thus no interaction of $MeCOCo(CO)_4$ and a nitrile was observed.

3.4. Preparation and characterisation of carboxyoleonitrile methyl esters by homogeneous cobalt catalysed methoxy-carbonylation reactions of oleonitrile.

3.4.1. Experimental

Oleonitrile (10g, 0.038 mol) and methanol (50ml) were mixed and then degassed prior to being syringed into the autoclave which contained dicobalt octacarbonyl (1.0g, 3 mmol) under a nitrogen atmosphere. The autoclave was then flushed with nitrogen and pressurised to 150 Bar with carbon monoxide. The system was heated to $170^{\circ}C$ for a period of ten hours and then left to cool. After depressurisation the contents were withdrawn and the crude mixture was shaken with dilute hydrochloric acid (10%) to remove the cobalt catalyst. The ester was solvent extracted with dichloromethane and the extracts washed with sodium bicarbonate solution and then water. The ester was separated from the impurities in the oleonitrile by column chromatography using a 50 cm column packed with Kieselgel 60 and eluted with ethylacetate/petroleum ether $40 - 60^{\circ}C$ in the ratio 40:60. The saturated nitrile impurities in the oleonitrile used eluted first followed by the ester fraction. The ester mixture was a colourless waxy solid mp $38 - 43^{\circ}C$ (10.5g, 86% yield).

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3.4.2. Characterisation

Analysis of the ester fraction by g.l.c. indicated the presence of more than one species with the main component being present in approximately 80%. This mixture could not be separated further due to the high boiling and chemically similar nature of the products, separation may have been accomplished by means of preparative scale h.p.l.c. but this was not available. The general formulae of the esters formed is:-

$$CH_3(CH_2)_n CH(COOMe)(CH_2)_m CN$$
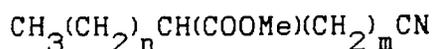
were for the predominant species n, m will be 7 and 8.

Infra-red analysis of the waxy solid was consistent with a fatty acid methyl ester giving a peak at 1730 cm^{-1}, for the carbonyl group, and a characteristic three band set at 1165, 1195 and 1255 cm^{-1} arising from -C(O)O- vibrations. The nitrile stretching frequency band was also prominent at 2245 cm^{-1}.

^{1}H and ^{13}C n.m.r.

^{1}H peak assignment:-

peak centre ppm	assignment	splitting	relative intensity
3.64	MeO	singlet	3
2.34	CH$_2$CH$_2$CN	triplet	(see text)
1.63	CH$_2$CH$_2$CN	doublet of triplets	2
1.26	CH$_2$'s	broad	24
0.88	Me	triplet	3

The peak due to the -CH$_2$CHCH$_2$- proton was thought to be hidden
  COOMe

under the α-proton peak as these environments give about the

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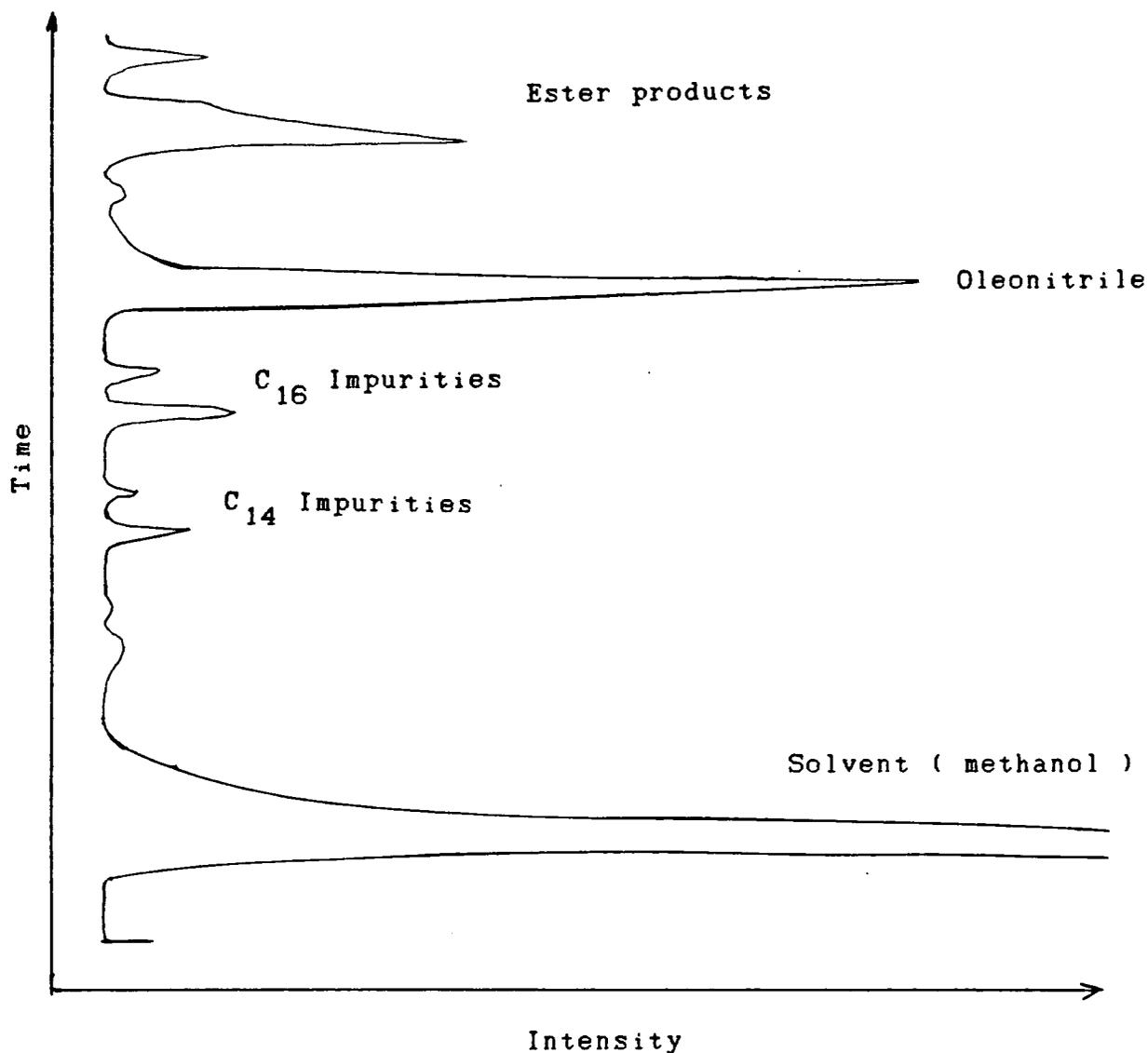
Typical g.l.c. trace for product mixture of methoxycarbonylated oleonitrile.

Column OV-101 (10% on Chromosorb G)

Conditions:- Injector temperature 270°C

Initial temperature 170°C for 5 min.

Increase at 10°C/min to 280°C

Detector temperature 290°C

Detector used was a flame ionisation detector

same shift, however the combined intensity being equivalent to the expected four protons. No indication of aldehyde, acid or acetal products were found in the ^{1}H n.m.r. spectrum.

^{13}C peak assignment

It is possible to calculate the expected shift of a substituted carbon in the ^{13}C n.m.r. spectrum (11a). The method uses a base shift for the hydrocarbon skeleton with an effect added for the particular functional group bonded to that carbon atom. For the purpose of this compound a decane skeleton can be used. An internal CH_2 group has an inherent shift of 30.5 ppm, thus a CH group with a carboxylic acid side group will have a shift of 30.5 + 17 = 47.5 ppm as the effect of a carboxylic acid group is 17 ppm. Using this method the following shifts can be calculated:-

$$\overset{\beta}{-CH_2}\overset{}{CH_2}\overset{\alpha}{\underset{\underset{COOH}{|}}{CH}}\overset{\beta}{CH_2}CH_2-$$

α-CH = 30.5 + 17 = 47.5 β-CH_2 = 30.5 + 2 = 32.5

also $\overset{\beta}{-CH_2}\overset{\alpha}{CH_2}CH_2CN$
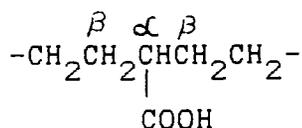
α-CH_2 = 14.2 + 4 = 18.2 β-CH_2 = 23.2 + 3 = 26.2

Peaks due to these groups are found in the ^{13}C n.m.r. spectrum at 49.6, 33.5, 18.6 and 28.3 ppm with the $\geq\underline{C}$HCOOH carbon being a close set of peaks at 45.7 to 45.3 ppm. Other prominent peaks are observed at 51.3 and 51.1 ppm due to the MeO- group, 119.7 ppm due to the C≡N functionality and a set of acid/ester carbonyl carbons at 173.9, 176.6, 176.7 and 177.0 ppm. These close grouping sets of peaks arise because of the different isomers. Although there is no indication in the ^{1}H n.m.r. for a

terminal carboxy group the ^{13}C gives peaks close to the

calculated shift values for such a species. In each of the ester

and C̲H-COOR groups one peak predominates. However use of direct

area ratios to obtain information of the relative numbers of

carbon atoms are not dependable due to Nuclear Overhauser

effects which give false peak areas.

Mass spectral data

The mass spectrum of compounds of these types are

difficult to obtain, in part due to their low volatility. Mass

spectra obtained by electron impact do not give the molecular

ion but instead show loss of the ester group to leave a cyano

alkane fragment m/e 264. The molecular ion was observed when

chemical ionisation was used, via isobutane as the ionising

media. The mass spectra then showed fragments at m/e 324 due to

[MH]$^+$ the molecular ion, m/e 293 [MH - OMe]$^+$ and m/e 265 [MH -

COOMe]$^+$, after this the spectra gave no useful fragmentation:

This is common in spectra obtained via chemical ionisation.

Conclusion

The ester functionality has been introduced into

oleonitrile to give high yields of carbonylated products,

typically 90%. However the position of substitution could not be

determined. The only indication of isomer distribution was the

appearance of two peaks in the g.l.c. trace (at m/e of 323),

the second peak due to the higher boiling component being

present as a minor component in the product mixture. Other

components separated by g.l.c. could not be identified. In the

mass spectrometer they gave peaks equivalent to oleonitrile plus

28 mass units, which corresponds to a carbonyl group, but these compounds are only present in small quantities. Other esters were prepared via similar procedures but were more difficult to separate and were not obtained sufficiently pure for analysis. G.l.c mass spectroscopy confirming them as the corresponding esters.

3.5. High pressure study of the cobalt/alcohol/oleonitrile system

3.5.1. Experimental

The investigation consisted of a series of experiments to determine the effects of catalyst type, concentration, physical reaction parameters, and the effect of various co-reactants on the alkoxycarbonylation of oleonitrile. The reactions were carried out in a 150 cm^3 Rockhurst autoclave (Fig. 2.2. Chapter 2). Product analysis was carried out routinely by g.l.c.

A general example of an experimental run is as follows:- dicobalt octacarbonyl (1.0g, 3.0 mmol) was placed into the autoclave against a counter current of dry nitrogen. The system was then sealed and flushed out with nitrogen several times. A solution of oleonitrile (10g, 0.038 mol) in methanol (50ml) was syringed into the autoclave and again the system flushed out with nitrogen. The autoclave was then pressurised to the required pressure (100 to 200 Bar) with carbon monoxide, heated to its set temperature where final adjustments were made to the pressure. The sytem was then left at reaction temperature for 5 hours with no more adjustments to pressure. After cooling overnight the system was depressurised and samples withdrawn for

g.l.c. analysis.

The effect of varying the reaction parameters was studied with respect to changes in molar conversion and molar selectivity. These parameters are defined as:-

% molar conversion = $\dfrac{\text{Moles of Oleonitrile converted}}{\text{Moles of Oleonitrile charged}}$ * 100

% molar selectivity = $\dfrac{\text{Moles of reactant converted to ester}}{\text{Moles of Oleonitrile converted}}$ * 100

Catalyst

The catalyst used throughout the study of the basic reaction was dicobalt octacarbonyl. Although industrially this is not the most suitable source of cobalt it was chosen because the actual catalyst is believed to be derived from this complex. This procedure therefore avoids any induction period which may occur as a consequence if a cobalt (II) salt is used, e.g. cobalt acetate. Under reaction conditions the salt is thought to be converted to a carbonyl species, but this process generally requires the use of higher temperatures (12).

3.5.2. Discussion

(a) The effect of reaction time

The effect of reaction time is shown in Table 3.1. and in Figure 3.1. From the graph it can be seen that the molar conversion increases linearly with time after an initial induction period. This indicates that the overall reaction rate is zero order with respect to the olefin oleonitrile as its concentration drops during the experiment. This result has also been found for other olefins, Ercoli (13) found that methoxycarbonylation of cyclohexene is approximately zero order

Table 3.1.

The effect of time on the methoxycarbonylation of oleonitrile

Sample No.	Time min.	Alkene Conversion %	Ester component 1	component 2	Selectivity %
1	0	-	-	-	-
2	15	1.5	-	-	-
3	30	5.1	97.7	2.3	97.7
4	45	11.0	96.1	3.9	99.1
5	60	18.3	94.9	5.1	98.5
6	75	25.9	92.9	7.1	97.6
7	105	38.9	91.3	8.7	96.6
8	130	49.3	88.4	11.6	95.5
9	190	68.7	87.4	12.6	95.6

Conditions:- Dicobalt octacarbonyl (1g, 3mmol), oleonitrile (4g, 0.015mol) methanol (60ml), 170°C, 200 Bar CO
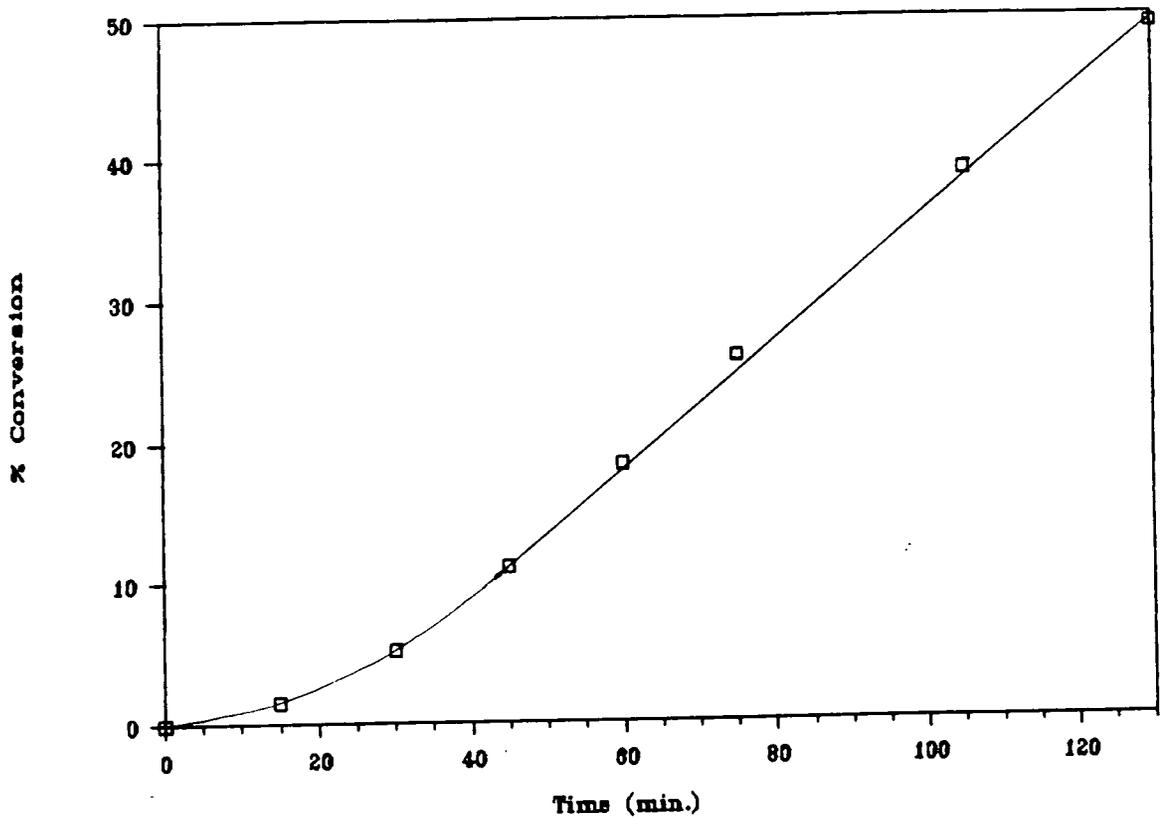
Figure 3.1. The effect of time on % conversion
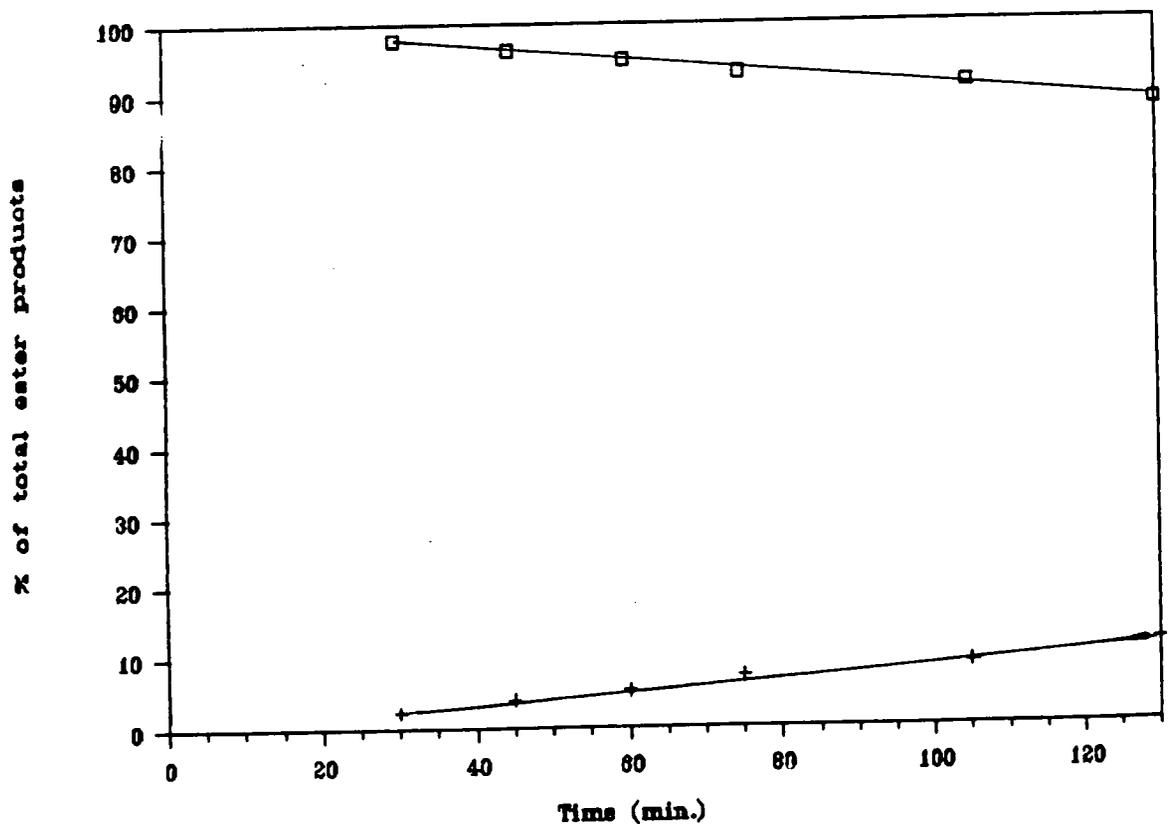
Figure 3.2. The effect of time on ester composition

with respect to olefin. Matsuda (14) agreed with this result

but also found that the order changes to approximately one when

pyridine is used as a co-reactant. The explanation of the zero

order of the olefin must be that the olefin is not involved in

the rate determining step, hence the rate constant for the

reaction

$$RCH = CHR' + HCo(CO)_3 \xrightarrow{Ka} RCH_2-\underset{\underset{Co(CO)_3}{|}}{CHR'}$$
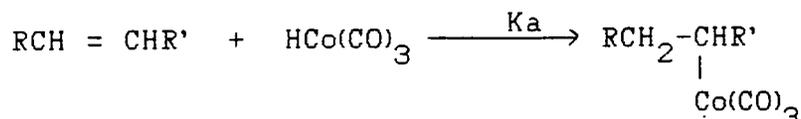
must be large with respect to subsequent rate constants. The

change in rate and increase in order with respect to olefin on

the addition of pyridine can be explained if it is assumed that

the cleavage of the acyl complex is originally rate limiting but

on the addition of pyridine the formation of the acyl species

becomes the rate limiting step:-

i.e.
$$RCH_2-\underset{\underset{Co(CO)_3}{|}}{CHR'} \longrightarrow RCH_2-\underset{\underset{Co(CO)_4}{|}}{CHR'} \xrightarrow{fast} RCH_2-\underset{\underset{\underset{Co(CO)_3}{|}}{CO}}{CHR'}$$

$$RCH_2-\underset{\underset{\underset{Co(CO)_3}{|}}{CO}}{CHR'} \xrightarrow{fast} RCH_2-\underset{\underset{\underset{Co(CO)_4}{|}}{CO}}{CHR'} \xrightarrow{Kb, ROH} RCH_2-\underset{\underset{COOR}{|}}{CHR'}$$
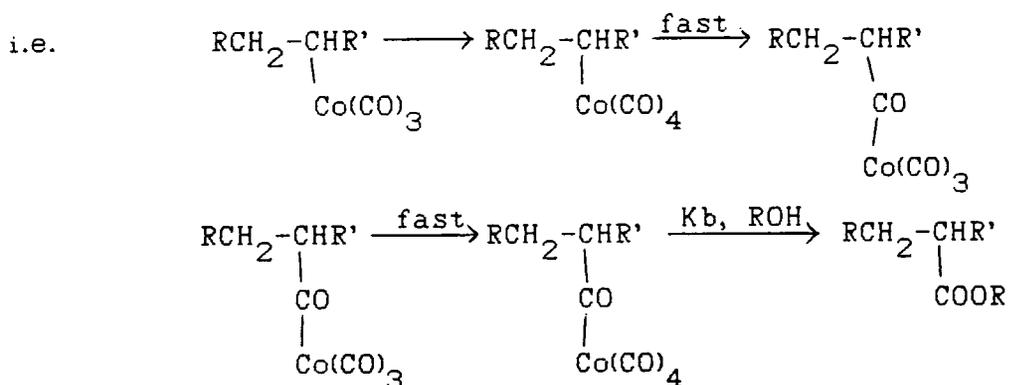
Hence if $K_a \gg K_b$, reaction rate is dependant on the

alcoholysis step, however if $K_b \gg K_a$ reaction rate is dependant

on the alkene interacting with the hydrido cobalt tricarbonyl.

Many of the above steps are in fact equilibria, however rapid

equilibration between acyl and alkyl species is known with the

acyl species being dominant. The reverse steps in many of the

reactions require the liberation of a carbon monoxide ligand.

Due to the large pressure of carbon monoxide in the system this process will be suppressed. For similar reasons it is to be expected that the reaction of the co-ordinatively unsaturated tricarbonyl species with carbon monoxide should be enhanced with increasing carbon monoxide pressure.

Analysis of the ester composition also indicates that as the reaction proceeds more of the second ester component is detected in the reaction mixture (Figure 3.2.). This is to be expected if one postulates that the quantity of isomerised alkene, formed by addition/elimination of the hydrido cobalt tetracarbonyl species to oleonitrile, increases during the reaction and hence towards the latter stages these isomers will become of greater importance in the reaction mixture. This will lead to a number of different isomeric esters in the product mixture, however these will be very similar in boiling point and thus the g.l.c. column will not easily resolve these species. Although the starting alkene will have been isomerised the separate isomers will be very similar in nature and thus were not detected singly by g.l.c. However as the starting material is almost exclusively the cis isomer, then isomerisation will produce a mixture of cis and trans isomer which will give different [1]H n.m.r. spectra.

In the initial stages of the reaction (i.e. the first 30 minutes) the rate of reaction to form products is slower than in the latter stages. There appears to be an initial induction period, possibly when the cobalt species in solution are converted to the active catalyst, thought to be hydrido cobalt

tetracarbonyl. Another explanation is that, due to the high cobalt to oleonitrile ratio required for reasonable reaction rates, significant proportion of the oleonitrile may not be free but co-ordinated in the form of cobalt complexes, $[CoL_6]^{2+}$, or present as $RCOCo(CO)_4$ complex. These will not be detected by g.l.c. and hence due to the method of calculating yields, the true conversion of oleonitrile will be under-estimated. As the total quantity of compounds derived from oleonitrile detected will be lowered; then normalisation of oleic compounds, to the quantity of oleonitrile initially present, will artificially increase the proportion of oleonitrile left in the reaction mixture.

The decrease in selectivity with time must be due to relatively slow side reactions which can occur. For example, the formation of aldehydes which under reaction conditions will be converted to acetals:-

$$RCOCo(CO)_4 \; + \; [H] \longrightarrow RCHO$$

$$RCHO \; + \; R'OH \longrightarrow RCH{\overset{\displaystyle OR'}{\underset{\displaystyle OH}{<}}}$$

$$RCH{\overset{\displaystyle OR'}{\underset{\displaystyle OH}{<}}} \; + \; R'OH \longrightarrow RCH{\overset{\displaystyle OR'}{\underset{\displaystyle OR'}{<}}} \; + \; H_2O$$
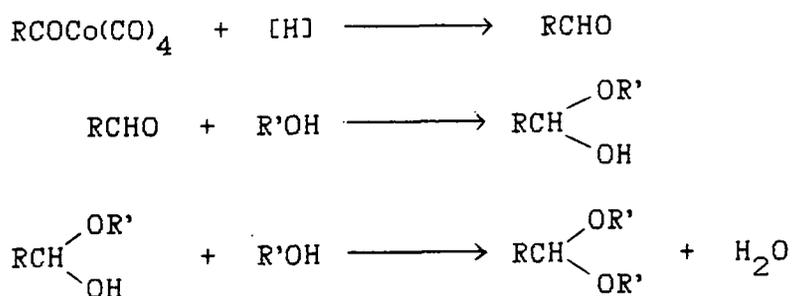
(b) Effect of metal concentration on the reaction

The effect of the metal concentration was determined by varying the amount of dicobalt octacarbonyl charged into the reactor. The results are shown in Table 3.2. and indicate an approximately half order with respect to metal concentration. Varying the metal concentration had little effect on the

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Table 3.2.

The effect of metal concentration on the methoxycarbonylation of oleonitrile

Sample No.	Time min.	Run 1		Run 2		Run 3	
		Yield mol	% Selectivity	Yield mol	% Selectivity	Yield mol	% Selectivity
1	30	3.8×10^{-4}	98.1	5.5×10^{-4}	97.6	7.8×10^{-4}	97.7
2	45	5.8×10^{-4}	96.8	1.0×10^{-3}	95.1	1.67×10^{-3}	99.1
3	60	1.16×10^{-3}	95.3	1.75×10^{-3}	94.1	2.79×10^{-3}	98.5
4	75	1.49×10^{-3}	92.9	2.43×10^{-3}	93.2	3.94×10^{-3}	97.6
5	105	2.66×10^{-3}	92.2	3.92×10^{-3}	92.2	5.92×10^{-3}	96.6
6	130	3.53×10^{-3}	90.9	5.08×10^{-3}	91.1	7.5×10^{-3}	94.6

Rate=3.39×10^{-5} mol/min   Rate=4.78×10^{-5} mol/min   Rate=8.85×10^{-5} mol/min

Moles $Co_2(CO)_8 = 7.29 \times 10^{-3}$ Moles $Co_2(CO)_8 = 1.47 \times 10^{-3}$ Moles $Co_2(CO)_8 = 2.92 \times 10^{-3}$

Average order with respect to cobalt concentration = 0.51

Average rate constant = 1.33×10^{-3} mol/min/mol$^{-\frac{1}{2}}$ Hence $K(obs) = 1.33 \times 10^{-3} \times [Co]^{0.51}$
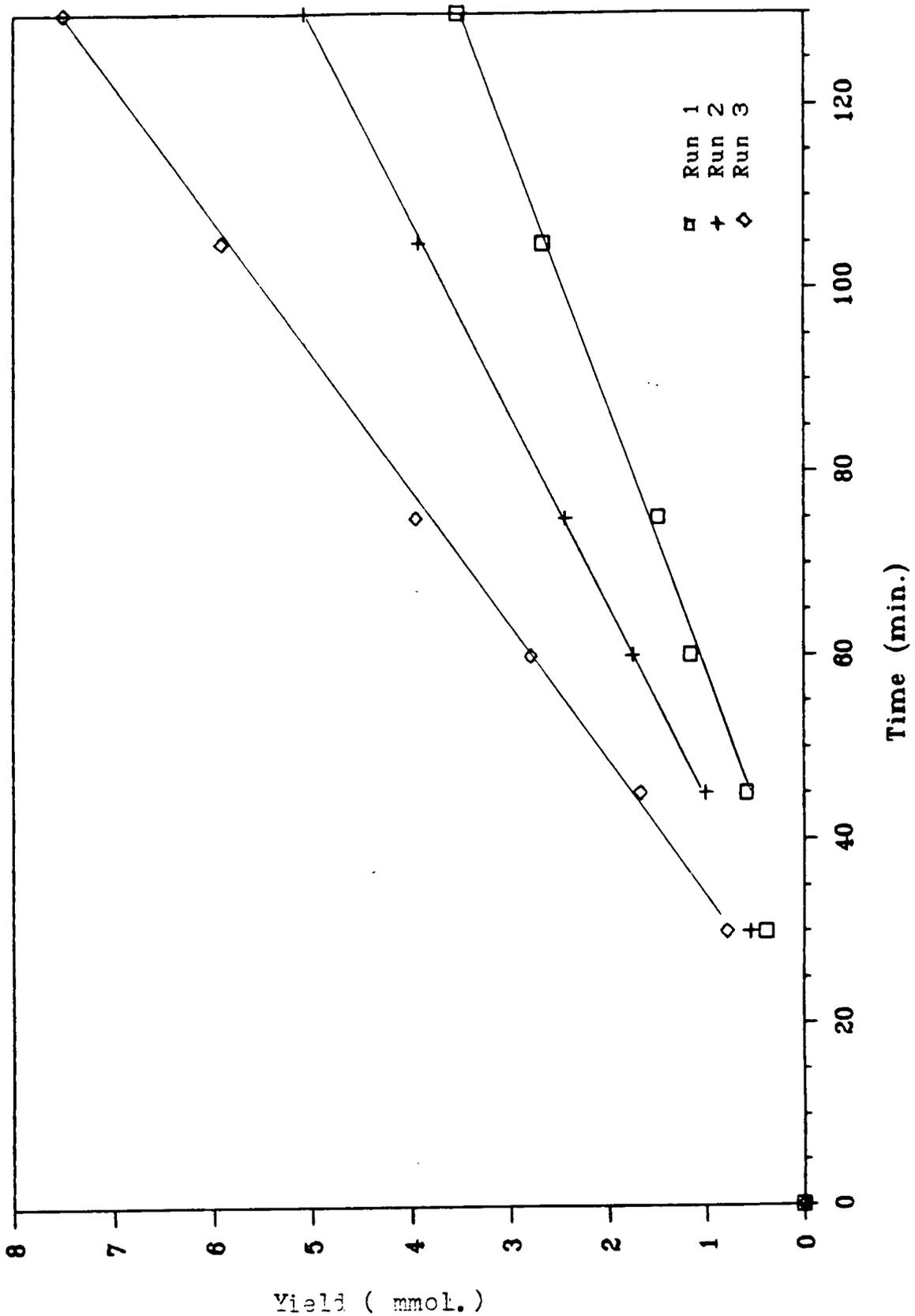
Figure 3.3. The effect of concentration of cobalt
on the rate of carbonylation of oleonitrile

selectivity or the composition of the ester fraction. A slightly higher selectivity was obtained at lower cobalt concentrations, but as detailed above, the selectivity was found to decrease as the amount of oleonitrile converted increased.

Thus it is not surprising that in the slower reactions, i.e. lower conversion in a given time, the selectivity is greater than the faster runs with higher cobalt concentrations. A similar effect was observed for the ester composition; the slower reaction producing a greater proportion of one component. This is presumably due to a smaller degree of isomerisation in the slower reactions.

Analysis of the results indicates that the reaction is about half order with respect to the cobalt concentration (correlation being about 0.9 for the data points). This agrees with studies by other workers on cyclohexene (13) and propene (15) and is similar to the order observed for acid synthesis. The rate constant is not very large as would be expected for an internal olefin, and internal alkoxycarbonylation is known to be slower than hydroformylation (16).

3.6. A study of the catalytic activity of salts of the
       tetracarbonyl cobaltate (-1) anion

Aim:- to determine the catalytic activity of the $Co(CO)_4^-$ ion. This species is present in large amounts in alcoholic cobalt carbonyl solutions.

3.6.1. Experimental

The basic experimental procedure was similar to that detailed above in section 3.5.1. Experiments with the non-air

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sensitive $PPNCo(CO)_4$ salt were performed by placing all of the reactants into the autoclave, flushing out the system with nitrogen and pressurising with carbon monoxide. In the other experiments the sodium salt was used. This salt was prepared by standard methods involving sodium amalgam reduction of a solution of dicobalt octacarbonyl in t.h.f. (2). In these experiments a solution of all the reactants was prepared under a nitrogen atmosphere, then syringed into the autoclave which had previously been flushed out with nitrogen several times. The system was then pressurised with carbon monoxide.

In each case after the required time at reaction temperature the system was allowed to cool; samples were then taken for g.l.c. analysis and infra-red analysis after depressurisation of the autoclave.

3.6.2. Discussion

The results from this series of experiments are given in Table 3.3. The amount of $PPNCo(CO)_4$ salt used (0.3g, $4.3*10^{-4}$ mol) was chosen to be equivalent to the amount of $Co(CO)_4^-$ generated from the complete dissociation of dicobalt octacarbonyl with a Lewis base (0.1g, $3*10^{-4}$ mol) so that a comparison with the preceding work could be achieved.

As can be seen from the results in Table 3.3., only low yields of esters were obtained. In each case for the temperature study the yield of ester was 4-6%. Increasing the temperature has the effect of increasing the conversion but decreasing the selectivity. The net result of both these effects is a drop in the yield of esters as the temperature is increased. Although

the results given here indicate poor yields, it was found in the

first experimental attempts artifically higher yields could be

obtained i.e. about 29% conversion. However after two or three

runs, using $PPNCo(CO)_4$ as catalyst, this dropped to the levels

recorded. These initially higher yields are ascribed to the

presence of cobalt (II) salts as impurities on the stirrer and

autoclave walls. Using the rate constant derived earlier (

section 3.5.), contamination was calculated to be equivalent to

using $2.1*10^{-6}$ mol of dicobalt octacarbonyl as catalyst. These

cobalt (II) salts together with $Co(CO)_4^-$ may undergo a reverse

of the dissociation reaction to produce dicobalt octacarbonyl (

17):-

$$8CO \ + \ 4Co(CO)_4^- \ + \ 2CoL_6^{2+} \longrightarrow \ 3Co_2(CO)_8 \ + \ 12L$$
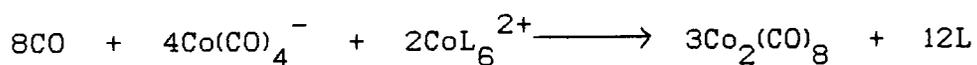
The cobalt (II) salts may also undergo direct reduction to

dicobalt octacarbonyl as the temperature is increased through

hydrogen impurities in the carbon monoxide would enhance this

process. Catalysts using cobalt (II) salts alone generally

require higher temperatures usually $200-220^{o}C$ (12). It was

thought that the cobalt (II) ion may act as an activator towards

hydrogen abstraction from methanol. The positive ion will

polarise the O-H bond, of co-ordinated methanol molecules making

the hydrogen more acidic and hence easier to abstract. The

methoxy ion thus generated will also be co-ordinated to the

cobalt (II) ion which is energetically more favourable than a

solvated species. Other ions may be expected to operate in a

similar manner. The results, however, show that this hydrogen

activation mechanism cannot play an important role in this

Table 3.3

Methoxycarbonylation of oleonitrile using $PPNCo(CO)_4$

Run	Reaction Time (h)	$PPNCo(CO)_4$ mol	Temperature °C	Pressure Bar	% Conversion	% Selectivity	Ester Component 1	Component 2
1	5	3.895×10^{-4}	160	160	6.4	85.2	59.8	40.2
2	5	3.895×10^{-4}	170	160	6.4	83.3	60.1	39.9
3	5	3.891×10^{-4}	180	160	6.6	68.2	60.8	39.2
4	5	3.892×10^{-4}	190	160	7.1	56.9	61.7	38.3
5	5	3.889×10^{-4}	200	160	8.2	52.8	62.5	37.5
6	5	3.891×10^{-4}	170	180	6.3	83.8	60.5	39.5
7	5	3.887×10^{-4}	170	200	6.5	82.5	60.9	39.1
8	5	3.896×10^{-4}	170	220	6.2	84.3	59.1	40.9
9	5	3.889×10^{-4}	170	240	6.5	84.5	59.9	40.1
10	5	3.892×10^{-4}	170	260	6.4	82.5	61.8	38.2
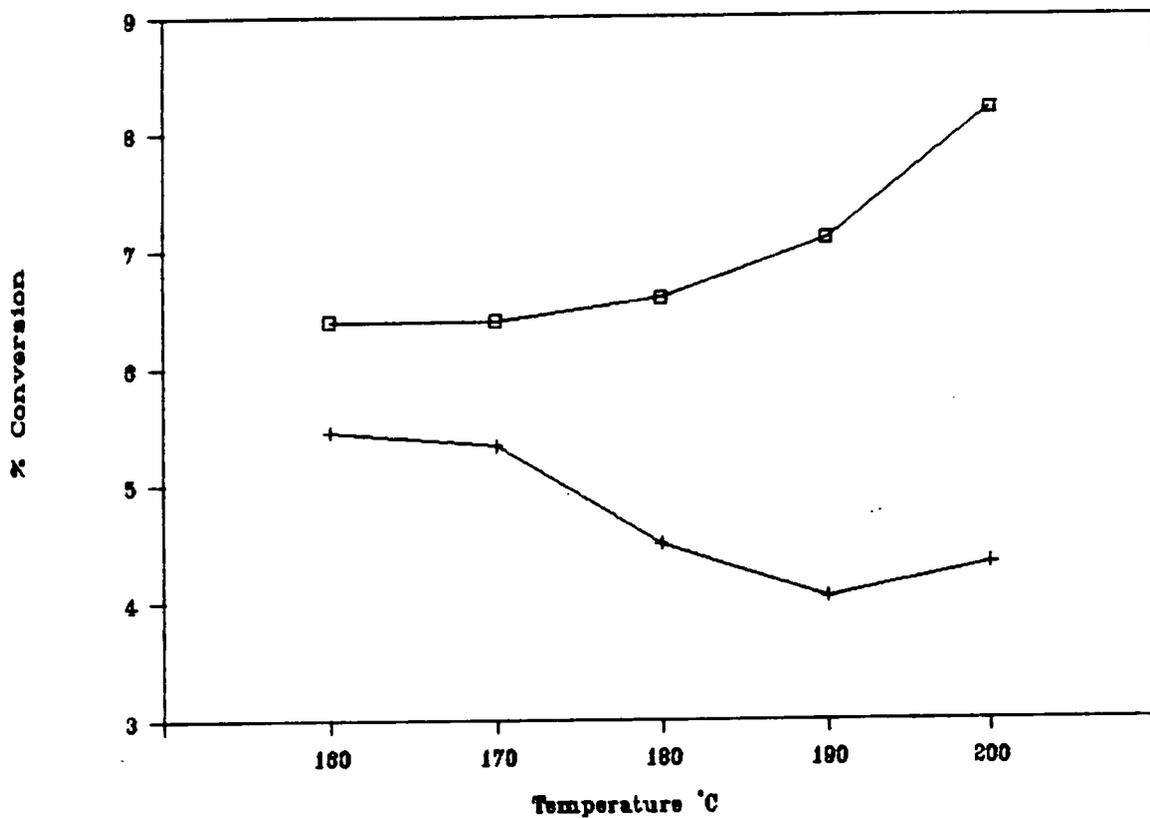
Figure 3.4a. The effect of temperature on the acivity of PPNCo(CO)$_4$
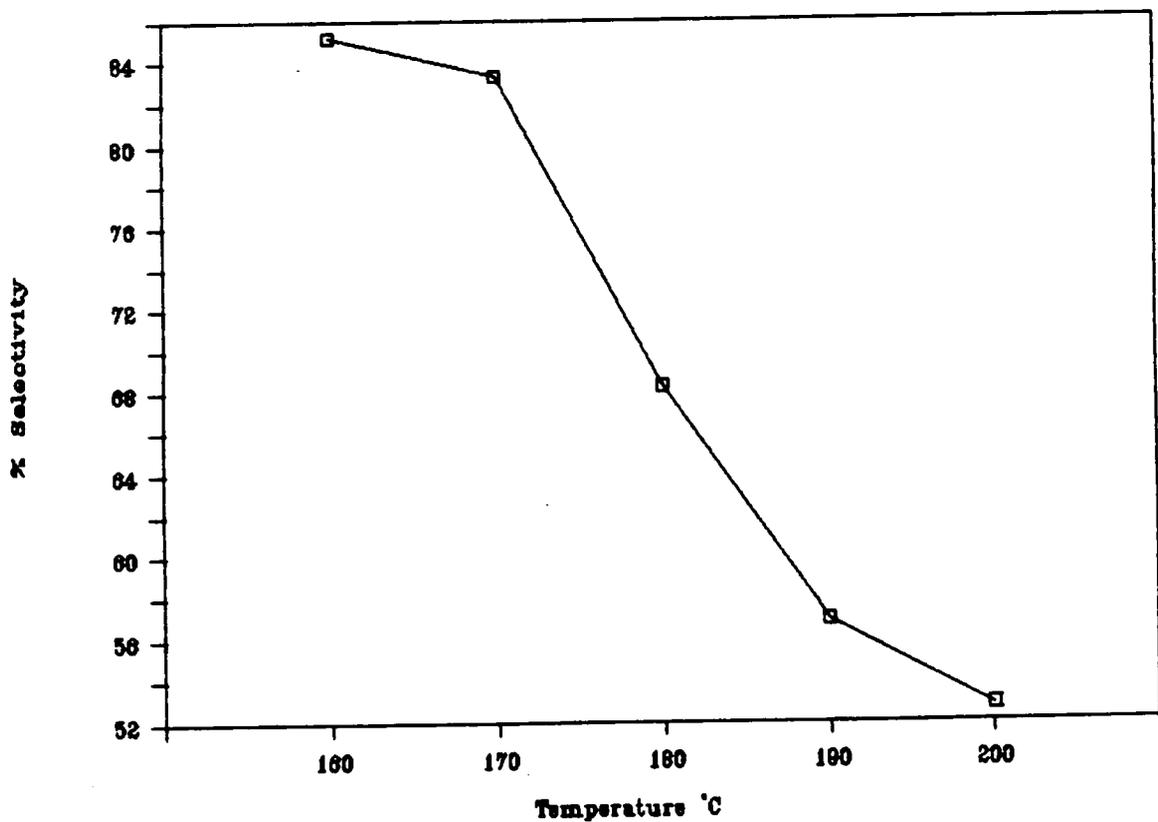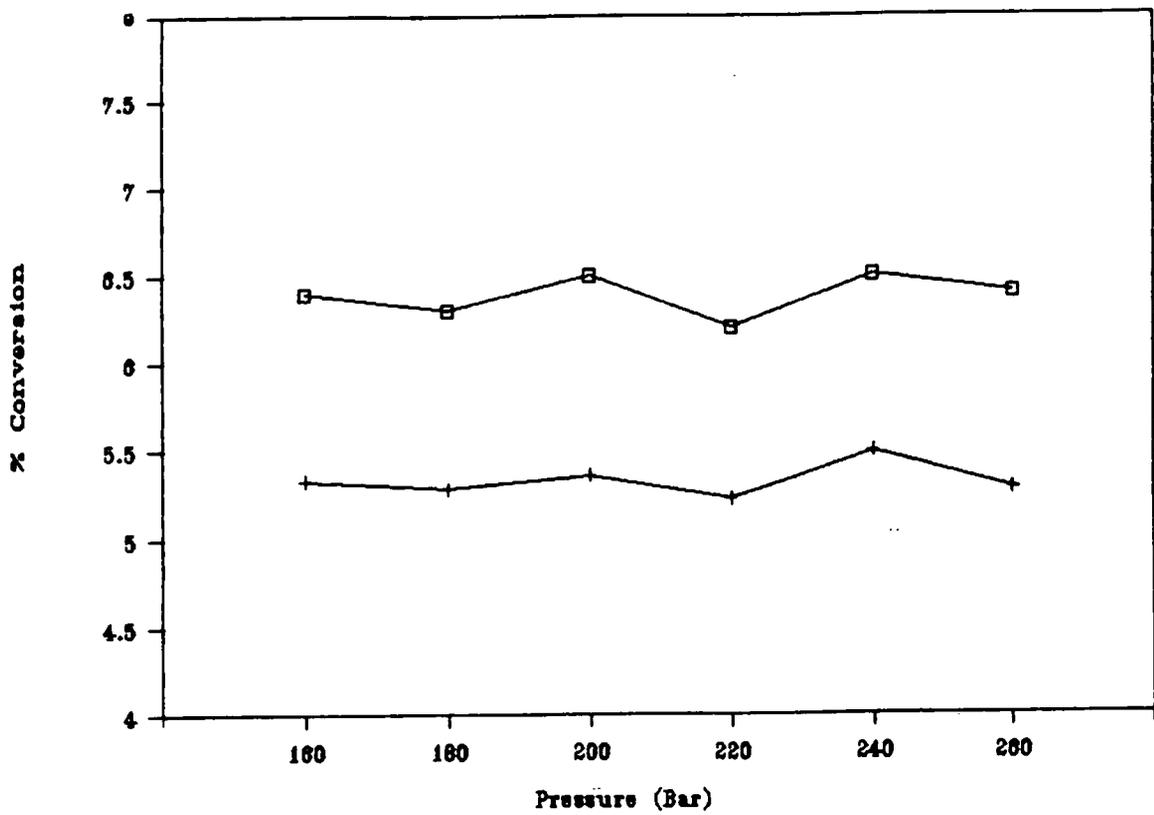
Figure 3.4b. The effect of pressure on the acivity of PPNCo(CO)$_4$
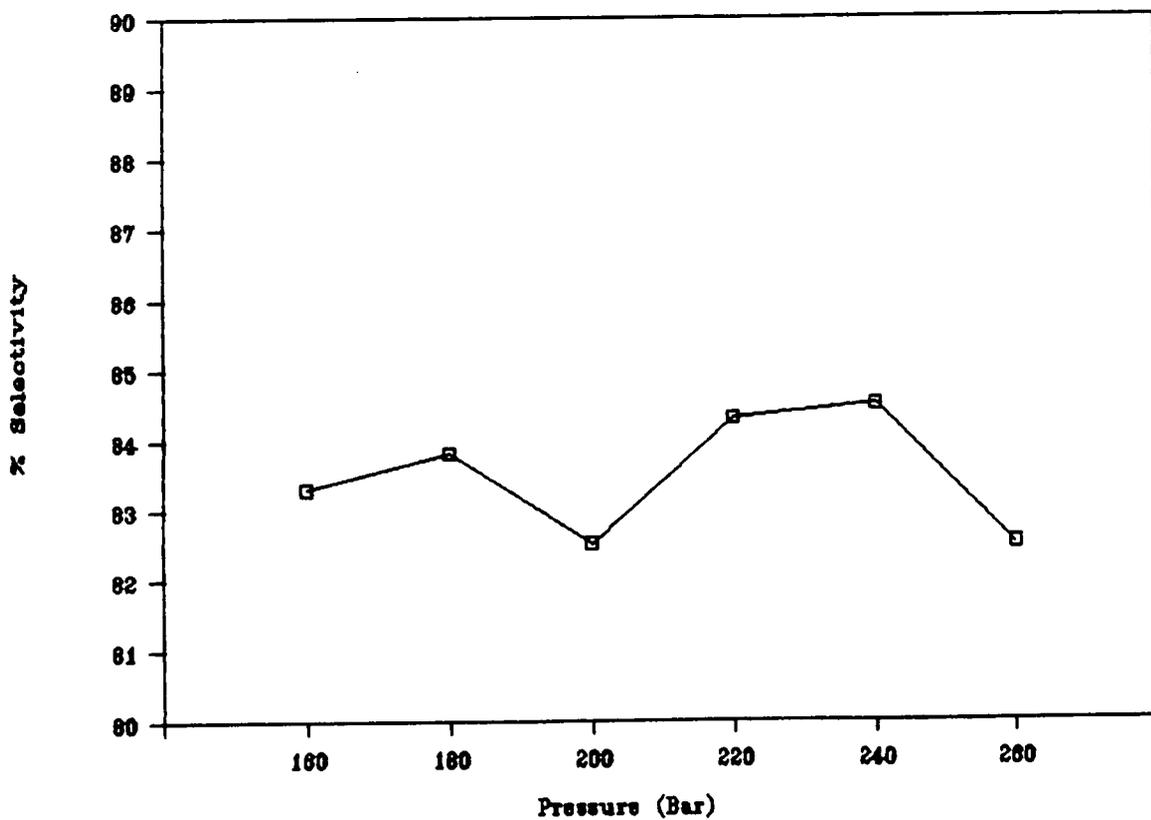
reaction as the metal salts e.g. $FeCl_3$ introduced with $NaCo(CO)_4$ give no enhancement of ester yield. The tripositive ions should in fact be more effective at this process than the cobalt (II) case, but this was not found to be the case. The effect of Co^{2+}/Co^{-1} concentration will be discussed later in Chapter 4.

The effect of pressure has no discernable effect on the reaction, however the yields recorded may not be sufficiently high or of sufficient precision to highlight any trends.

CHAPTER THREE - REFERENCES

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CHAPTER FOUR

METHOXYCARBONYLATION OF OLEONITRILE

AND HEX-1-ENE IN THE PRESENCE OF

VARIOUS ADDITIVES

Introduction

The main work detailed in this chapter is concerned with the basic alkoxycarbonylation of hex-1-ene, together with the effect of co-reactants on the methanol oleonitrile system. Hex-1-ene was chosen to give a greater insight into the mechanism due to the ease of analysis of the isomeric nature of the products formed which is not possible with oleonitrile. The two systems will be compared to see if the nitrile functionality has any discernible effect on the reaction mechanism.

4.1. A study of the methoxycarbonylation of Hex-1-ene

Aims:- to ascertain the effect of temperature and pressure on the composition of the residual hexenes and on the isomer distribution in the ester products.

4.1.1. Experimental

The basic experimental procedure is as described earlier in the basic oleonitrile methoxycarbonylation reaction. A general example is as follows:-

Hex-1-ene (3.5g, 0.043mol) was dissolved in methanol (16ml) the resulting solution was degassed and syringed into the autoclave, which contained dicobalt octacarbonyl (0.05g, 0.15mmol) under an inert nitrogen atmosphere. The system was flushed out, pressurised with carbon monoxide to the required pressure, and heated to the set temperature and allowed to react for 5 hours; after cooling overnight a sample was withdrawn for analysis. The sample was first vacuum transfered to remove all non-volatile materials prior to analysis using capillary column g.l.c. Product identification was made on the basis of retention

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time on the g.l.c. column, and through the use of g.l.c. linked

mass spectrometry. This allowed identification of the different

methyl hexanoate isomers by the prominent peak in the mass

spectrum, due to the Mc-Lafferty rearrangement:-
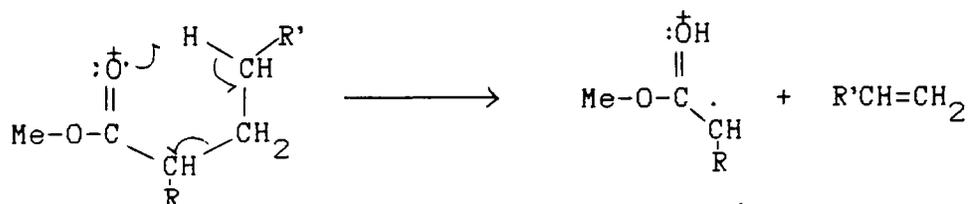
This rearrangement is very facile and forms the base peak for

straight chain methyl esters from C_6 to C_{26}. Identification of

this peak in the mass spectrum allows the nature of the R group

to be determined, and hence the position of the carbonyl group in

the ester. In the present case ,i.e. for hex-1-ene, the straight

chain isomer (methyl heptanoate) gave a base peak in the mass

spectrum of m/e 73 due to the $[MeOCOCH_2{}^{\cdot}]^+$ species formed by the

Mc-Lafferty rearrangement. Similarly 2-methyl hexanoate gave a

base peak at m/e 88 and 2-ethyl pentanoate at m/e 102.

4.1.2. Discussion

The study of these experiments are presented in Table 4.1.

The study undertaken was carried out to give some indication of

the effects of temperature and pressure on the methoxy-

carbonylation of hex-1-ene, but not to give a detailed

examination of these parameters as regards the yields and

selectivity towards ester formation.. As can be seen from the

table the use of cobalt catalysts based on the $Co(CO)_4{}^-$ ion does

not give any significant yield, as was found with oleonitrile in

Chapter 3 section 3.6. The results also indicate that increasing

Table 4.1.

Methoxycarbonylation of hex-1-ene

Catalyst	Quantity mmol	Temperature °C	Pressure Bar	% Conversion	% Selectivity	n/(n+iso)
PPNCo(CO)$_4$	0.14	175	280	trace	–	–
PPNCo(CO)$_4$	0.14	200	200	trace	–	–
PPNCo(CO)$_4$	0.14	175	280	trace	–	–
Co$_2$(CO)$_8$	0.14	150	200	1.6	92.3	0.614
Co$_2$(CO)$_8$	0.14	175	200	5.2	85.2	0.628
Co$_2$(CO)$_8$	0.14	200	200	6.7	82.1	0.636
Co$_2$(CO)$_8$	0.14	175	160	3.6	88.9	0.572
Co$_2$(CO)$_8$	0.14	175	240	11.4	–	–

Conditions:- Hex-1-ene 3.5g, 0.043mol

Methanol 16ml

5 hours

the total pressure of the reaction gives an increase in yield of ester products, however, there is also a slight decrease in the selectivity of the reaction towards ester production. An increase in pressure also has the effect of decreasing the amount of branched products as indicated by the increase in the ratio of the amount of the straight chain isomer (n-isomer) to total amount of ester products. This effect is also found with hydro-formylation. However, in these systems under typical hydroformylation conditions branched products can be obtained even when the parent olefin is not isomerised (1). This precludes the mechanism of sequential addition/elimination of hydrido-cobalt tetracarbonyl as the route to branched products. The explanation of this phenomena postulates that isomerisation of the alkyl chain occurs while the olefin is bound to the cobalt in the form of a π-complex, the resulting σ-bonded complex then undergoes further reaction and does not generate free olefin by elimination of hydrido-cobalt tetracarbonyl. This type of mechanism is only applicable at carbon monoxide pressures above 50 atm and temperatures below $120^{\circ}C$. In the present reaction the temperatures used are sufficiently high to allow sequential addition/elimination of the hydrido species to occur, this leads to a highly isomerised mixture of hexenes in the final product mixture.

4.2. The effect of the Co(II)/Co(-1) ratio on the
       methoxycarbonylation of hex-1-ene

Aim:- to determine the effect of varying the Co(II) to Co(-1) ratio on the yield and composition of the esters produced.

4.2.1. Experimental

The catalyst for this series of experiments consisted of a mixture of $PPNCo(CO)_4$ and anhydrous cobalt (II) acetate. The catalyst mixture was placed into the autoclave, along with methanol (16ml) and hex-1-ene (3.5g, 0.043 mol). The system was flushed out with nitrogen and the pressurised to 120 Bar with carbon monoxide. The autoclave was then heated to $200^{\circ}C$, the pressure adjusted to 200 Bar and left to react for 2 hours. On cooling and after depressurisation samples were taken for g.l.c. and infra-red analysis. The g.l.c. samples were treated as above in section 4.1.1.

4.2.2. Discussion

The quantity of $PPNCo(CO)_4$ used was chosen to be equivalent to the amount of $Co(CO)_4^-$ generated by the complete dissociation of 0.05g of dicobalt octacarbonyl into the disproportionation complex such that comparisons could be made with the results obtained in section 4.1.1. The choice of a mixture of the $PPNCo(CO)_4$ salt and a cobalt (II) salt for this study was made so as to avoid the possibility of other carbonyl species being initially present in the reaction mixture. It is not possible to ensure that all the dicobalt octacarbonyl has been converted in to the disproportionation complex before the reaction begins, thus a mixture of dicobalt octacarbonyl and a cobalt (II) salt in methanol was thought to be unsuitable for these experiments.

It is clear from the results for runs 1 and 2 in Table 4.2. and from the study with oleonitrile (Table 3.3 Chapter 3) that $Co(CO)_4^-$ by itself is not a very active catalyst. The slight

Table 4.2.

The effect of the Co^{-1}/Co^{2+} ratio on the methoxycarbonylation of hex-1-ene

Run	$Co(acetate)_2$ mol	$Co(CO)_4^-$ mol	% Conversion	% Selectivity	n/(n+iso)	$Co^{-1}:Co^{2+}$
1	—	1.95×10^{-4}	< 0.5	—	—	—
2[a]	—	1.96×10^{-4}	< 0.5	—	—	—
3	5.88×10^{-5}	1.93×10^{-4}	1.72	92.7	0.548	1:0.304
4	1.07×10^{-4}	1.94×10^{-4}	1.91	92.2	0.553	1:0.552
5	1.70×10^{-4}	1.97×10^{-4}	2.05	91.0	0.570	1:0.862
6	3.57×10^{-4}	1.96×10^{-4}	2.12	90.7	0.572	1:0.820
7[b]	$Co_2(CO)_8$ (1.46×10^{-4} mol)		6.70	79.1	0.636	1:0.500

Conditions:- 200 Bar CO
200°C for 2 hours
16ml methanol
3.5g, 0.043mol hex-1-ene

[a] Reaction as in 1 but 210°C

[b] Reaction carried out using dicobalt octacarbonyl as catalyst
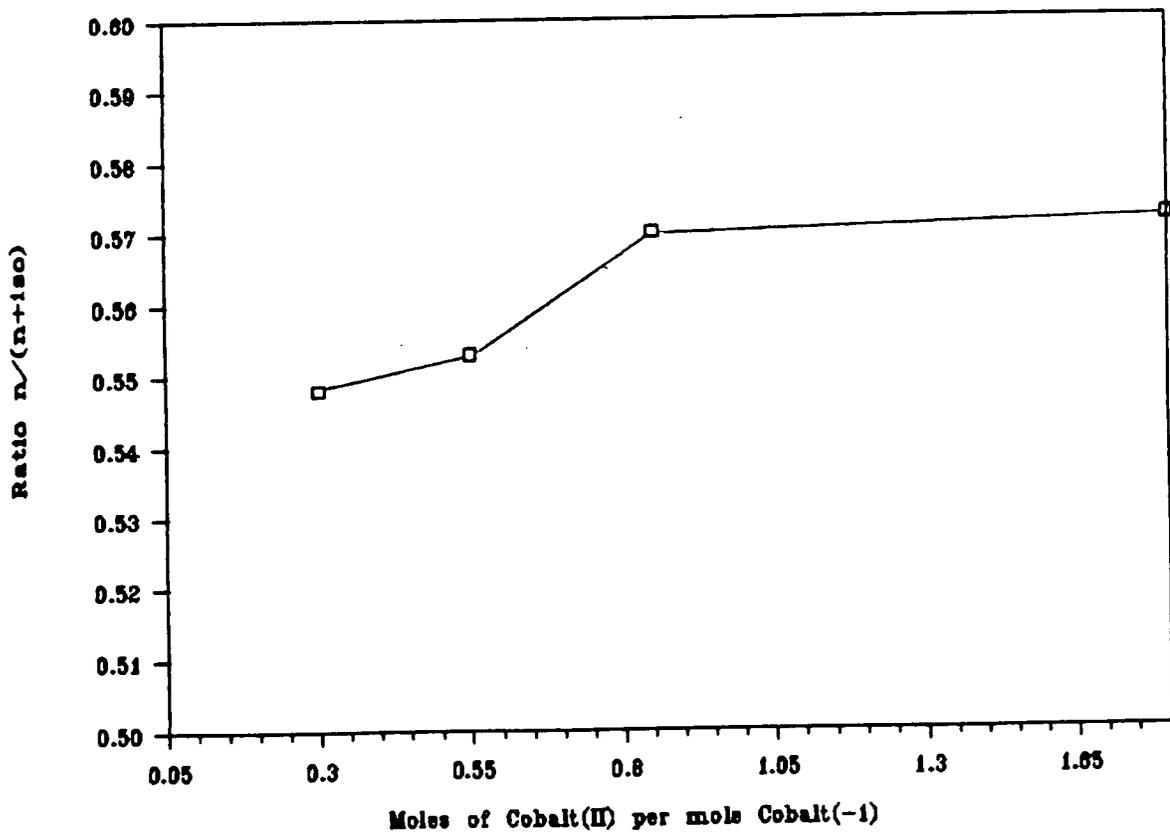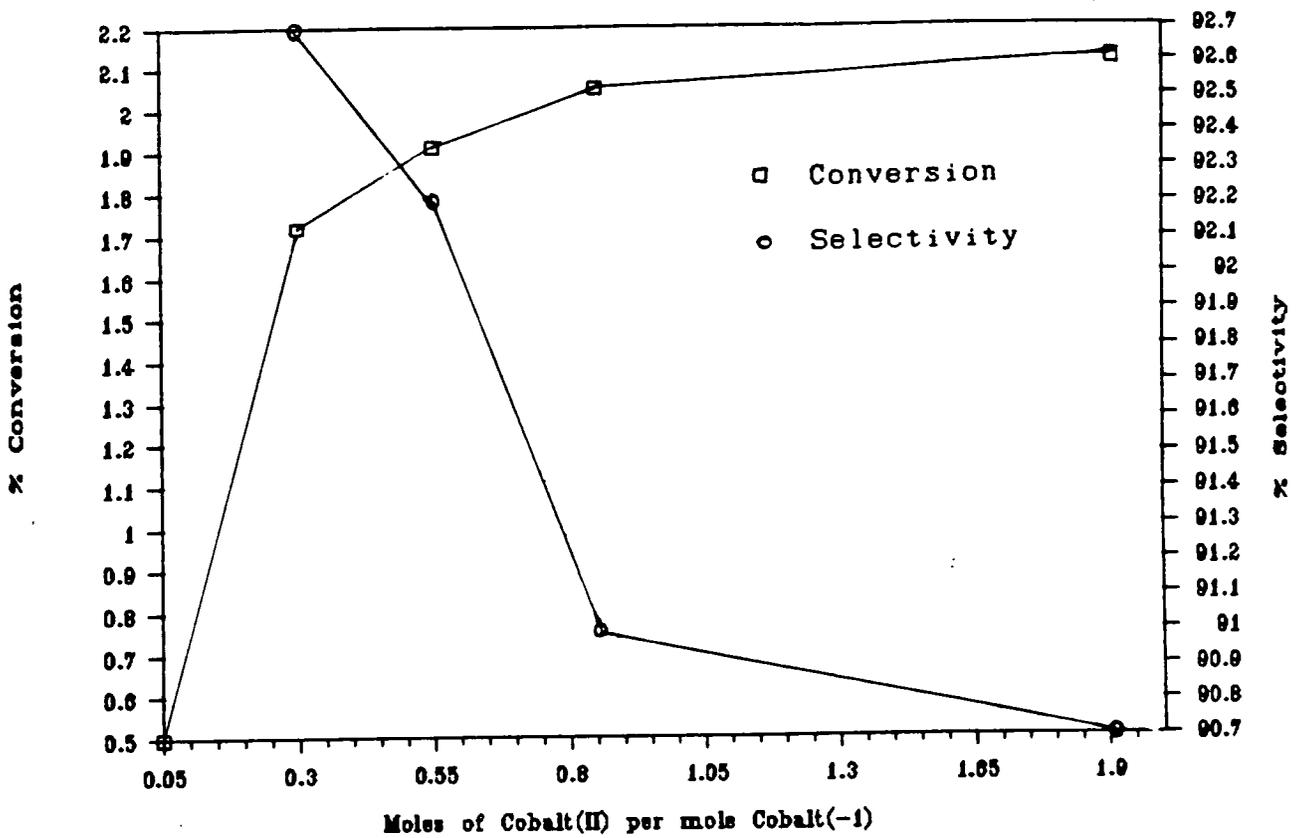
Figure 4.1. The effect of the Co(II)/Co(-1) ratio on the methoxycarbonylation of hex-1-ene

activity that is observed for this species may, in fact, be due only to trace impurities of cobalt (II) species, present either in the PPNCo(CO)$_4$ salt, or possibly on the walls of the reactor. The results here show that the introduction of cobalt (II) salts increase the conversion of alkene to ester products.

In the absence of a cobalt (II) species there is only a small yield of ester (i.e. < 0.5%) which increase to 1.7% when cobalt (II) acetate is added to the reaction mixture (run 3). Three main possibilities for the mode of action of the cobalt (II) counter ion can be envisaged; the first being activation of the alcohol towards hydrogen abstraction by co-ordination of the alcohol to the cobalt (II) ion, this will polarise the hydrogen oxygen bond making the hydrogen more acidic and hence easier to abstract. This explanation however is thought to be unlikely as the study with various other counter ions e.g. Fe^{3+} and Cr^{3+} have little or no effect on the yield (section 3.6. Chapter 3). These tripositive ions, however, should be better at this process than the cobalt (II) ion due to the increased polarity caused by the tripositive ion. Thus the following reaction is thought to be of little importance:-

$$\left[(MeOH)_5 Co \leftarrow \overset{\delta-}{\underset{\underset{H\delta+}{|}}{:O}} - Me \right]^{2+} \longrightarrow \left[(MeOH)_5 CoOMe \right]^{+} + H^{+}$$
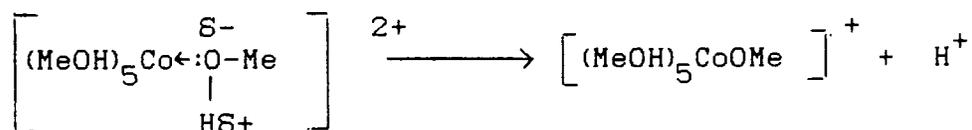
The second possible explanation involves the reduction of the cobalt (II) ion to cobalt (0), which in the carbon monoxide atmosphere will be converted into a carbonyl species. This process in known to occur as the methoxycarbonylation reaction can be achieved using cobalt (II) salts (2). These reactions

however generally require higher temperatures i.e. 230°C. One would, however, expect there to be a greater effect than that observed here on the yield if this process was occurring to any significant extent. Each successive reaction summarised in Table 4.2. has approximately double the amount of cobalt (II) acetate and since the reaction is abuot half order with respect to the cobalt concentration (for dicobalt octacarbonyl catalysed reactions section 3.5. Chapter 3), then run 6 should be about 2.5 times faster than run 3. However only an increase in yield of 1.23 fold was recorded and thus this process is considered to be unlikely.

The third explanation relies on the reversibility of the dissociation reaction of dicobalt octacarbonyl:-

$$3Co_2(CO)_8 \rightleftharpoons 4Co(CO)_4^- + 2Co(MeOH)_6^{2+} + 8CO$$
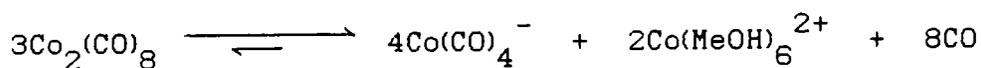
This reaction has been reported to be reversible by Orchin (3) and has been supported by Kilner (4). The catalyst derived from a mixture of Co(-1)/Co(II) salts, however is still not as active as the catalyst based on dicobalt octacarbonyl (i.e. 6.7% for the carbonyl derived catalyst c.f. 1.9% for the corresponding Co(-1)/Co(II) mixed catalyst). This could be due to reverse reaction being kinetically slow. Another possible explanation is that some dicobalt octacarbonyl may be required to "catalyse" the reverse reaction. It is known that in the preparation of dicobalt octacarbonyl, yields are often improved if some dicobalt octa-carbonyl is already present (5). This may also explain why the catalyst made from cobalt (II) and cobalt (-1) salts is not as active as a solution of dicobalt octacarbonyl, allowed sufficient

time to disproportionate. In the latter case there will be some carbonyl species still in the molecular form, as complete dissociation requires several hours at room temperature.

Infra-red analysis of the solutions resulting from the reactions detailed in Table 4.2. showed no new carbonyl stretching frequency absorptions, the only species observed being due to the $Co(CO)_4^-$ ion at 1900(vs) cm^{-1}.

4.3. The effect of molecular hydrogen on the methoxy-carbonylation of hex-1-ene

Aim:- to determine the effect of added molecular hydrogen on the rate and isomer distribution of the methoxycarbonylation reaction.

4.3.1. Experimental

Dicobalt octacarbonyl (0.1g, 0.3 mmol) was placed into the autoclave and the system sealed. After flushing the system out with dry nitrogen a solution of Hex-1-ene (6g, 0.07 mol) and methanol (15ml) was syringed into the autoclave and the system again flushed with dry nitrogen. Hydrogen was then admitted into the system to the required pressure, followed by nitrogen such that the total pressure of the two gasses was kept constant at 400 p.s.i. (27.5 Bar). The gas pressure was then increase to 115 Bar with carbon monoxide, after which no further adjustments were made to the pressure. The autoclave was then heated to 170°C during which the pressure increased to 180 Bar. The autoclave was stirred rapidly at this temperature for 1 hour after which it was allowed to cool and then depressurised. Samples were then withdrawn for g.l.c. mass spectroscopy, and

infra-red analysis; the g.l.c., samples were vacuum transfered before analysis to remove the catalyst.

4.3.2. Discussion

Analysis of the reaction mixture was complicated by the co-elution of the acetal of 2-ethyl pentanal and n-methyl heptanoate from the g.l.c. column. This prevented full analysis of the reaction mixture such that only the yield of the branched esters and the yield of 2-methyl hexanal and heptanal acetals could be determined. However these are sufficient to give an indication of the yield of esters vs. hydrogen concentration and the extent of isomerisation.

The results are shown in Table 4.3. and in Figures 4.2. and 4.3. It is clear from the g.l.c. results that a significant rise in the reaction rate is observed, even after the addition of relatively small amounts of hydrogen into the system; with almost complete conversion occurring when 400 p.s.i. of hydrogen is used. In these experiments the range of hydrogen pressures used, cover the conditions required for pure methoxy-carbonylation to pure hydroformylation, at high hydrogen pressures the reaction gives predominantly acetal synthesis (see Table 4.3.). The yield of acetals, formed from the reaction of the methanol solvent with an aldehyde, increases with increasing hydrogen concentration as expected:-

Table 4.3.

Run	Pressure of Hydrogen Bar	moles of Hydrogen	ratio Co:H_2	% Conversion of hexene	1-Methyl hexanoate mmol	1-Ethyl pentanate mmol	1,1-Dimethoxy heptane mmol	1-Methyl dimethoxy hexane mmol
1	27.2	0.149	1:509	100	1.12	0.67	25.2	16.1
						Ratio(2/(2+3))=0.63		Ratio(n/(n+2))=0.61
2	20.4	0.112	1:383	98.5	3.48	2.03	24.6	16.3
						Ratio=0.63		Ratio=0.60
3	13.6	0.074	1:253	94.7	3.90	2.10	23.5	16.6
						Ratio=0.65		Ratio=0.58
4	6.8	0.037	1:127	89.4	4.32	2.02	19.4	15.3
						Ratio=0.68		Ratio=0.56
5	1	0.0055	1:9.3	39.7	3.64	1.93	4.76	4.01
						Ratio=0.65		Ratio=0.54
6	0	<2x10^{-4}	1:0.7*	23.1	2.95	1.60	trace	trace
						Ratio=0.65		

Conditions :- Pessure see section 4.3.1.
hexene 6g, 0.07mol
dicobalt octacarbonyl 0.1g, 0.3mmol
170°C for 1 hour

* Amount of hydrogen is estimated
assuming 100 Bar CO with a
300 v.p.m. impurity of hydrogen
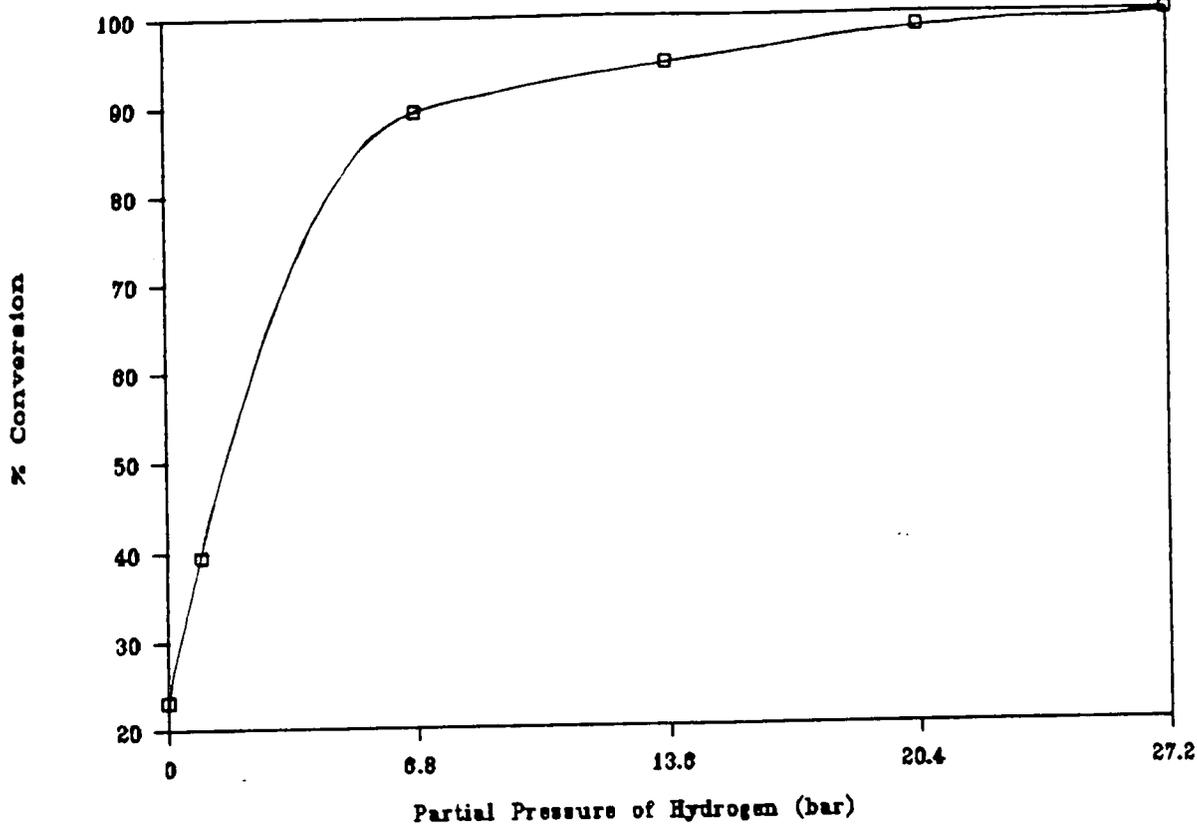
Figure 4.2. The effect of molecular hydrogen
on the % olefin conversion
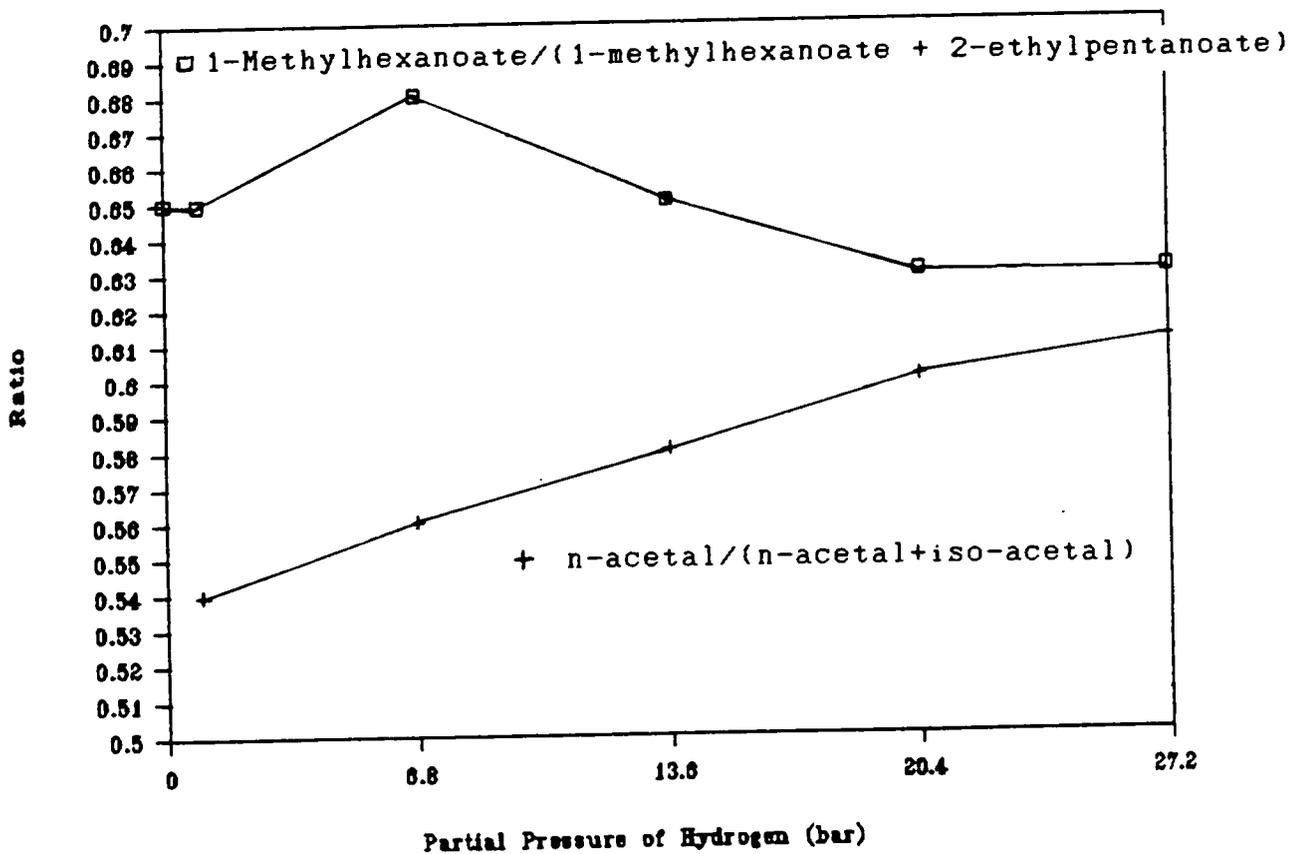
Figure 4.3. The effect of molecular hydrogen
on the isomer distribution

$$RCH=CH_2 \xrightarrow{\text{CO/H}_2} RCH_2-CH_2CHO$$

$$RCH_2-CH_2CHO + MeOH \longrightarrow RCH_2-CH_2\underset{\underset{OMe}{|}}{CH(OH)}$$

$$RCH_2-CH_2\underset{\underset{OMe}{|}}{CH(OH)} \longrightarrow RCH_2-CH_2CH(OMe)_2 + H_2O$$
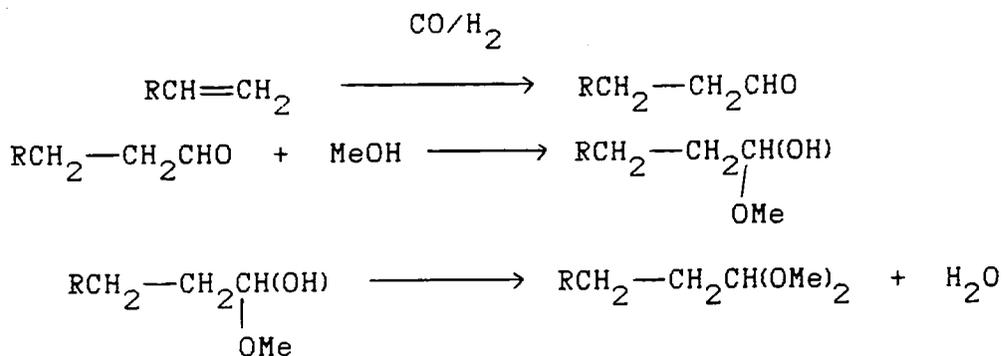
However as the hydrogen concentration increases the degree of branching is found to drop; i.e. the amount of heptanal acetal increases relative to the amount of 2-methyl hexanal acetal formed by reaction at the 1 and 2 positions in hex-1-ene respectively. This effect is indicated by an increase in the n/(n+iso) ratio. A corresponding increase in branching, as the hydrogen concentration decreases, has been noted in the hydroformylation of propene (6). In these systems the selectivity of the reaction towards the straight chain isomer is greater, which may be explained by the use of lower temperatures and pressures of carbon monoxide used in those systems. This effect, of increasing the degree of branching as the partial pressure of hydrogen drops cannot be easily explained. One postulation is that more than one catalytic species is present and the relative proportions of each are dependant on the hydrogen partial pressure.

In the case of the ester products it is not as easy to determine any changes in the degree of branching, since the yield of the straight chain isomer could not be determined. However the yields of 2-methyl hexanoate and 2-ethyl pentanoate could be determined, resulting from reaction at the 2 and 3 positions in

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hex-1-ene. If the quantity of the straight chain isomer increased relative to the total amount of ester products, then there would also be an expected increase in the quantity of 2-methyl hexanoate relative to 2-ethyl pentanoate, although to a smaller extent than for the straight chain isomer. However in the present system no discernible trend was observed, as evidenced by the ratio of 2-methyl hexanoate to 2-methyl hexanoate plus 2-ethyl pentanoate, on increasing the hydrogen pressure. This may suggest that, unlike the acetal synthesis case above, the degree of branching is independent of the partial pressure of hydrogen. This would indicate that the methoxycarbonylation and hydroformylation reactions are not as mechanistically similar as it first appears. The other explanations are that any trend was too small to be detected, or that the ratio of the 2-methyl hexanoate to the 2-methyl hexanoate plus 2-ethyl pentanoate isomers does not parallel the n/(n+iso) ratio.

It can be seen that relatively small amounts of hydrogen have a significant effect on the reaction rate. By increasing the pressure of hydrogen by a factor of 7 the yield increases by 52%. A smaller effect is observed on going from no added hydrogen to flushing the system out with hydrogen (run 5 Table 4.3.). As indicated, also in Table 4.3., the carbon monoxide used contains 300 vpm (typically) of hydrogen, which is equivalent to a cobalt to hydrogen molar ration of 1:0.7. Under the condition employed this may be sufficient to initiate a catalytic cycle. The hydrogen may react with dicobalt octa-carbonyl to give hydrido cobalt tetracarbonyl (I) directly or it may help in the

conversion of cobalt (II) salts to active cobalt (O) species.

4.4 The effect of additives on the methoxycarbonylation of

hex-1-ene

Aim:- to determine the effect of various co-reactants, such as alkyl and alkali metal halides, on the yields and selectivity towards ester production.

4.4.1. Experimental

Solid co-reactants e.g. potassium iodide (0.5g, 3 mmol) were placed with dicobalt octacarbonyl (0.05g, 0.146 mmol) into the autoclave. The system was then flushed with nitrogen. A solution of hex-1-ene (3g, 0.035 mol) in methanol (50ml) mixed with any liquid co-reactants, were syringed into the autoclave. The system was then treated as in section 4.1.1., the reaction temperature being 200°C with the initial pressure being 200 Bar carbon monoxide. Samples were analysed as previously described.

4.4.2. Discussion

The results are tabulated in Table 4.4.; each additive will be discussed separately. Firstly the addition of pyridine has a dramatic effect on the yield of esters. An increase from 5.2% to 44.5% was obtained, accompanied by a slight increase in the selectivity towards the straight chain ester. The rate increase achieved by the addition of some tertiary amines, like pyridine and quinoline, has been noted previously by several authors (7,8,9) and two explanations have been given for the mode of action of these bases. The first explanation is that pyridine assists in the cleavage of the acyl cobalt tetracarbonyl species.

This species can be regarded as being similar to an acyl halide, in certain reaction mechanisms, and a similar accelerating effect is in fact also observed in base assisted hydrolysis of acyl halides (10). This has been explained by the formation of a pyridinium complex as an intermediate in the hydrolysis:-

$$RCOCo(CO)_4 \ + \ py \ \longrightarrow \ RC \overset{O}{\underset{N^+C_2H_5}{<}} \ + \ Co(CO)_4^-$$

$$\overset{R-C}{\underset{ROH}{\overset{O}{\diagdown}}} \ \longrightarrow \ RCOOR' \ + \ py \ + \ H^+$$
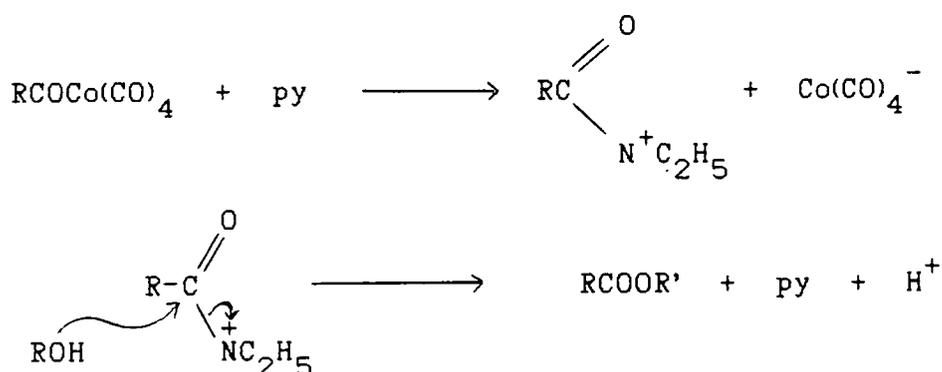
An increase of 10^5 in the rate of hydrolysis of acetyl or benzoyl chlorides can be achieved by the addition of pyridine.

The second explanation was proposed by Matsuda (11) who suggested that the addition of pyridine causes a new cobalt pyridine carbonyl complex to be formed; this complex is then postulated to be a more efficient catalyst. The disadvantage in this explanation is that pyridine will react with dicobalt octacarbonyl, in the same fashion as methanol, and produce the disproportionation product $[CoL_6][Co(CO)_4]_2$, which should possess the same activity as the catalyst in methanol. The first explanation seems to be more reasonable in the present context.

The second co-reactant employed was methyl iodide. It was found that this will react with dicobalt octacarbonyl to give the methyl cobalt tetracarbonyl initially, which converts rapidly to the acyl species (see section 3.3. Chapter 3). The acyl cobalt tetracarbonyl complex may be expected to undergo reaction to

Table 4.4.

The effect of additives on the methoxycarbonylation of hex-1-ene

Additive	Quantity mol	% Conversion	% Selecivity	n/(n+iso)
-	-	6.7	82.1	0.636
I_2	1.46×10^{-4}	1.6	89.9	0.578
KI	2.90×10^{-4}	3.3	82.0	0.577
MeI	1.00×10^{-2}	0.59	84.1	0.606
Pyridine	1.00×10^{-2}	44.5	85.1	0.696

Conditions:- $Co_2(CO)_8$ 0.05g, 0.146mmol

Hex-1-ene 3g, 0.035mol

200^oC, 200 Bar CO

produce methyl ethanoate in a similar reaction to the methoxycarbonylation of alkenes:-

$$MeCo(CO)_4 \xrightarrow{\text{MeOH}} MeCOOMe + HCo(CO)_4$$
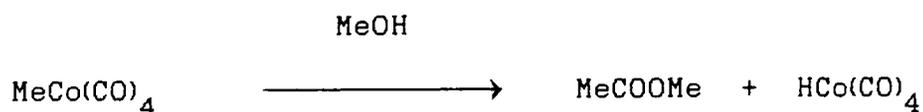
The hydrido cobalt tetracarbonyl thus generated may be expected to undergo further reaction and produce ester products derived from hex-1-ene. However a slight drop in yield is observed from 5.2%, with no methyl iodide, to 2.0% with methyl iodide. This may be explained by postulating a similiar mechanism to that proposed for homologation of methanol in the presence of methyl iodide (12).

$$Co(CO)_4^- + MeI \longrightarrow MeCo(CO)_4 + I^-$$
$$MeCo(CO)_4 + CO \longrightarrow MeCOCo(CO)_4$$
$$MeCOCo(CO)_4 + H_2 \longrightarrow MeCH_2OH + HCo(CO)_4$$
$$HCo(CO)_4 + OH^- \longrightarrow Co(CO)_4 + H_2O$$
$$MeOH + I^- \longrightarrow MeI + OH^-$$
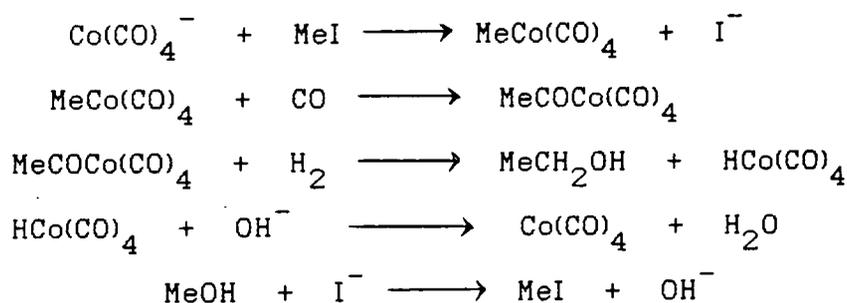
Evidence for methyl iodide was found by g.l.c. mass spectroscopy, in the product mixture. Also present in the product mixture were light boiling products derived from methanol, but these were not identified.

The other additives used were iodine and potassium iodide. In each case a decrease in yield was noted, the effect being less with potassium iodide. In the case of iodine (which was added to the methanol/hex-1-ene mixture before syringing into the autoclave) it was hoped that 1,2 addition to the double bond in hex-1-ene would occur to give 1,2 diiodohexane, which would react by nucleophilic attack of the $Co(CO)_4^-$ ion, to give an acyl

species via an alkyl cobalt tetracarbonyl:-

$$CH_3(CH_2)_4CHICH_2I + Co(CO)_4^- \longrightarrow CH_3(CH_2)_4CHICH_2Co(CO)_4$$
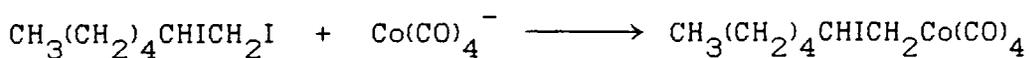
Unfortunately it seems that the iodine preferentially reacted

with the dicobalt octacarbonyl to give CoI_2. In the case of

potassium iodide, the yield also decreased possibly due to the

iodide ion catalysing the disproportionation of dicobalt octa-

carbonyl to form the CoX_4^{2-} species (13). In both cases

products derived from methanol were again observed, although to a

lesser extent than in the methyl iodide case. It therefore seems

likely that the iodide ions reacted in a similar manner to those

in the methyl iodide case above to produce methyl iodide. In each

of the iodine containing systems the isomer distribution

indicated a slight increase in the amount of branched isomers.

This may be due to the slower carbonylation reaction allowing a

greater degree of olefin isomerisation of an initial π-complex.

4.5. The effect of co-reactants on the methoxycarbonylation of

    oleonitrile

4.5.1. Experimental

The reactions were carried out using a similar procedure to

that detailed in the previous section, except that reactions were

performed at 200 Bar initial pressure of carbon monoxide and at

$180^{\circ}C$ for 5 hours.

4.5.2. Discussion

As can be seen from the results in Table 4.5., the use of

crude un-distilled oleonitrile in place of the purified material

causes a decrease in yield of esters obtained and a slight

decrease in selectivity is also found. These effects may be

expected as crude oleonitrile can contain acids, amides, dienes, amines and acetylenes as impurities, albeit in small quantities, and are due to the method of manufacture in most cases. This involves conversion of oleic acid to the amide followed by dehydration to the nitrile. The polyenes and acetylenes are present in small quantities in the natural glycerides from which oleic acid is obtained. Acetylene compounds are known to be effective catalyst poisons (14) by selective removal of dicobalt octacarbonyl:-

$$Co_2(CO)_8 \longrightarrow \longrightarrow Co_2(CO)_6(RC-CR')$$
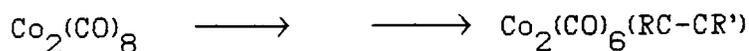
The acetylene bridges the two cobalt atoms and forms a relatively stable compound. The nitrile group is also known to bond through the π-system (15) but these derivatives are not as stable as those which involve σ-bonding through the nitrogen atom.

The addition of a small quantity of water to the reaction mixture seems to have very little effect on the reaction rate, a slight increase being noted. The increase in reaction rate could be due to two effects. The first is the production of hydrogen via the water gas shift reaction.

$$CO + H_2 \longrightarrow CO_2 + H_2$$

This reaction however is not catalysed by dicobalt octacarbonyl. The quantity of hydrogen required to affect the rate is not very large because a significant rise in reaction rate was observed on the addition of small quantities of hydrogen (see section 4.3.). The second effect, that could occur, is the more facile cleavage of the acyl cobalt tetracarbonyl; this could be due to the greater nucleophilicity of water compared to methanol or due

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to steric effects. The alkyl group formed from oleonitrile is quite bulky with long alkyl chains. These will tend to protect the carbonyl group from nucleophillic attack and since water is a smaller nucleophile its attack will be less hindered. The acid formed by this process will undergo reaction with the methanol solvent to regenerate water and form the ester.

The steric effect of the alkyl group may also explain the observed trend for methoxycarbonylation: Terminal alkenes react fastest, with branched internal alkenes the slowest (16). There is also a decrease in reaction rate on going from primary to secondary and tertiary alcohols. This trend was noted during the preparation of various esters (see section 3.4. Chapter 3). In the case of propanol and tertiary butanol a large amount of oleonitrile was unreacted, the tertiary butanol being the slowest to react.

There is however another explanation for these results – the alcohols themselves may undergo side reactions thus reducing their activity; the steric effect however is expected to still play an important part. One of the main side reactions is dehydration of the alcohol to give an alkene, a reaction which can not occur with methanol:-

$$CH_3CH(OH)CH_3 \longrightarrow CH_3CH=CH_2 + H_2O$$
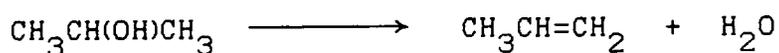
4.6. The effect of phosphorus ligands on the methoxycarbonylation of oleonitrile

Aim:- to determine the effect of different phosphine types and different phosphine complexes on the reaction.

Table 4.5.

Reactants	% Conversion	% Selectivity
Oleonitrile/methanol	52	90
Oleonitrile/methanol/pyridine	65	85
Oleonitrile/methanol/water	55	89
Oleonitrile/t-butanol	9	72
Crude oleonitrile/methanol	39	87

Conditions:- $Co_2(CO)_8$ 1.0g, 3 mmol

Oleonitrile 10g, 0.038 mol

180°C, 200 Bar CO, 5 hours

Table 4.6.

Catalyst	% Conversion
$Co_2(CO)_8/PPh_3$ 1:1	3.9
$Co_2(CO)_8/P(n-butyl)_3$ 1:1	2.8
$Co(CO)_3(PPh_3)_2.Co(CO)_4$	3.7
$Co(CO)_3(P(cyclohexyl)_3)_2.Co(CO)_4$	2.9
$[Co(CO)_3PPh_3]_2$	3.7
$[Co(CO)_3P(cyclohexyl)_3]$	2.7

Conditions:- Cobalt species 0.3 mmol

Oleonitrile 3g, 10 mmol

170°C, 200 Bar CO, 5 hours

4.6.1. Experimental

The basic experimental procedure can be split in to two methods depending upon the nature of the catalyst: For non-air sensitive samples the catalyst was placed into autoclave together with oleonitrile (3g, 10 mmol) and methanol (30ml). The system was flushed out with nitrogen several times, followed by pressurisation to 200 Bar with carbon monoxide. The reaction was stirred rapidly at 170°C for 5 hours and then allowed to cool overnight. After depressurisation samples were taken for g.l.c. analysis and any solid formed was filtered off, washed with methanol and dried 'in vacuo'. The solids were analysed by elemental analysis and infra-red spectroscopy.

For air sensitive samples the catalyst was placed into the autoclave, which had previously been flushed out with nitrogen, against a counter current of nitrogen. The system was then sealed and flushed out. A solution of oleonitrile (3g, 10 mmol) in methanol (30ml) was prepared and degassed by freeze-thaw cycles. The solution was then syringed into the autoclave and the experiment carried out as above.

4.6.2. Discussion

The general result of the addition of a phosphine ligand to the system is a dramatic decrease in the yield of ester products (see Table 4.5.). This effect did not seem to show any dependence on the type of complex used or on the nature of the phosphine ligand. As a representitive example the results for the triphenylphosphine systems will be discussed in more detail.

In this study three types of phosphine systems were used

these were:-

$$[Co(CO)_3(PPh_3)_2]^+[Co(CO)_4]^-, \quad [Co(CO)_3PPh_3]_2, \quad Co_2(CO)_8/PPh_3$$
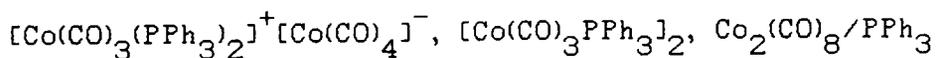
              (I)   (II)

In each case only a low yield of ester products were obtained with no new organic species being detected. In each reaction a red/brown solid was obtained from the reaction mixture, this precipitate gave infra-red peaks at 1960(m), 1950(s) and 1905(w) cm^{-1} in the carbonyl stretching frequency region. These peaks can be assigned to the $[Co(CO)_3PPh_3]_2$ complex (peaks reported at 1960(sh), 1945(s) and 1900(w) cm^{-1} (17), the other possible complex $[Co(CO)_3(PPh_3)_2]^+[Co(CO)_4]^-$ gives peaks at 2008(m) and 1895(s) cm^{-1}). No other bands were observed in the solution infra-red except for the $Co_2(CO)_8/PPh_3$ system, which gave a peak at 1900 cm^{-1} due to the $Co(CO)_4^-$ species.

    Several publications have appeared in the past few decades on the reaction of phosphine ligands with dicobalt octacarbonyl (18,19). In general the only species stable at room temperature in the absence of a carbon monoxide atmosphere are the two complexes (I) and (II) above. The relative amount of each of these species formed by a reaction of phosphine and dicobalt octacarbonyl, is dependant mainly on the temperature. Complexes of type (I) are only favoured by low temperatures ($0^{o}C$) and polar media. The dimer $[Co(CO)_3PPh_3]_2$ is solely formed if the temperature is greater than $50^{o}C$. Thus it is not surprising that the runs with these two complexes are equivalent.

    In the case of the dicobalt octacarbonyl/triphenylphosphine system the complex that could be initially formed in solution is

the $Co_2(CO)_7PPh_3$ species, this type of complex is generally only stable under carbon monoxide atmospheres, and is usually in equilibrium with other species (20). With no carbon monoxide atmosphere these species are unstable and disproportionate to the dimer (II) and dicobalt octacarbonyl:-

$$2Co_2(CO)_7PPh_3 \longrightarrow Co_2(CO)_8 + [Co(CO)_3PPh_3]_2$$
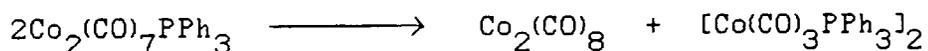
Thus even if this species was present under reaction conditions disproportionation will have occurred on depressurisation to give the dimer (II). The remaining dicobalt octacarbonyl will itself disproportionate in the reaction media to give the $Co(CO)_4^-$ /CoL_6^{2+} complex.

The reason for the low activity for phosphine complexes for the alkoxycarbonylation reaction can be ascribed to two effects; namely low activity of the hydride species $HCo(CO)_3PPh_3$ and steric hindrance. The hydride complex is less reactive than the unsubstituted system due to the interaction of the cobalt and phosphorus atoms making the cobalt hydrogen bond less polar. The hydride species with trialkyl phosphorus ligands is a bulky group, and thus co-ordination of an alkene is harder than in the ligand free complex. Also the acyl species $RCOCo(CO)_3PPh_3$ will be sterically a very demanding molecule for nucleophilic attack of the carbonyl group by methanol to give the ester products.

CHAPTER FOUR - REFERENCES

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CHAPTER FIVE

AN INFRA-RED STUDY OF THE

ALKOXYCARBONYLATION REACTION AND

DISCUSSION OF THE REACTION MECHANISM

5.1. Introduction

The following chapter is split into two sections; the first part details the high pressure infra-red spectroscopic study of the alkoxycarbonylation reaction. The second section deals with a detailed examination of the alkoxycarbonylation reaction with critical discussion of each reaction step, comparisons being drawn with other cobalt based catalytic reactions.

In recent years infra-red and combined infra-red/ultra violet spectroscopic studies have been reported for the hydroformylation reaction, a reaction which has mechanistically related steps to the hydrocarbonylation and alkoxycarbonylation reactions. However neither of these latter systems have been examined under 'in situ' conditions. The investigation of the hydroformylation of 1-octene by Whyman using dicobalt octacarbonyl (1), indicated that the main cobalt species present under reaction conditions were dicobalt octacarbonyl and the acyl cobalt tetracarbonyl complex. These results were supported by Mirbachs et al combined infra-red/ultra-violet examination (2). This work indicated that the rate limiting step of the reaction was hydrogenolysis of the acyl complex. Whyman, however, reported that in the case of internal alkenes the reaction is limited by the initial reaction of the alkene with the hydrido cobalt tetracarbonyl complex.

5.2. High pressure infra-red study of the cobalt/methanol/ alkene alkoxycarbonylation system

Aim:- to observe under reaction conditions the major cobalt species present in the reaction.

5.2.1. Experimental

The infra-red study was carried out using the equipment previously described in Chapter 2 (see section 2.4. Fig 2.1.). The general experimental procedure was as follows:- dicobalt octacarbonyl (0.5g, 1.5 mmol) was placed into the sample cell, which had previously been flushed with dry nitrogen. A degassed mixture of oleonitrile (4g, 1.5 mmol) and methanol (16ml) was then syringed into the sample and reference cells against a counter current of nitrogen. The system was then sealed, flushed with nitrogen, then pressurised to 100 Bar with carbon monoxide. The infra-red spectra were recorded at regular temperature intervals of approximately $25^{\circ}C$ - at each temperature the system was allowed 30 minutes to reach equilibrium before the final spectra were recorded (i.e. no change with time was observed in the infra-red spectrum). On reaching the required reaction temperature (typically $170^{\circ}C$) the pressure of the system in some cases was increased and the infra-red spectrum recorded. The system was usually left to react at the required temperature for abuot 1 hour, after this period the cell was allowed to cool. Again as the temperature decreased the infra-red spectrum was recorded at various intervals, allowing time for the system to equilabrate. Finally after depressurisation, at room temperature, the last infra-red spectrum was recorded.

5.2.2. Results and discussion

(a) Dicobalt octacarbonyl/methanol/alkene system

After half an hour at room temperature and 100 Bar pressure the only peak detectable in the 2200 to 1500 cm^{-1} region of the

infra-red was at 1895(vs) cm^{-1}, due to the Co(CO)$_4^-$ ion. Increasing the temperature had the effect of decreasing the intensity of the peak, but no new carbonyl bands were detected until the reaction temperature was above 125$^{\text{o}}$C. At this temperature the infra-red showed peaks at 1995(m), 1890(vs) and 1710(m) (broad) cm^{-1}. On increasing the temperature the peak at 1710 became stronger and a shoulder at 2040 cm^{-1} was also evident. On cooling no change in these peaks were noted.

In the case of hex-1-ene, as the alkene reactant, the infra-red spectra initially showed peaks at 2040(sh,m), 2010(m), 1895(m) and 1840(m) cm^{-1}. On increasing the temperature the peaks at 1895 and 1840 cm^{-1} increased in intensity with the peak at 1895 cm^{-1} becoming weak above 125$^{\text{o}}$C. At 170$^{\text{o}}$C a new carbonyl peak appeared at 1710(m) cm^{-1}, increasing in intensity with time, and the absorption at 2010(m) cm^{-1} broadened. On cooling, the peaks at 1895 and 1840 cm^{-1} increased in intensity and remained unchanged even on depressurisation. At this stage a new carbonyl peak became visible at 2105 cm^{-1}.

The interpretation of the carbonyl stretching frequency region is complicated by the absorption of methanol at 2040 cm^{-1}. Although the spectrometer consists of both sample and reference cells it is difficult to match the path lengths, at high pressures and temperatures, to remove this peak. Even if the path lengths are equal at the start of the reaction the may change during the experiment. Also the spectrometer will not be very sensitive in this region as both the sample and reference beams will be attenuated by the methanol peak.

In both cases the infra-red spectra initially showed the strong absorption of $Co(CO)_4^-$ at 1895 cm^{-1} arising from the disproportionation of dicobalt octacarbonyl in methanol to form $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$. The other less intense peaks present at room temperature in the hex-1-ene reaction, could possibly be due to molecular dicobalt octacarbonyl (peaks reported at 2070(s), 2059(mw,sh), 2044(s,sh), 2042(s), 2031(m,sh), 2022(s), 2002(vw), 1866(mw,sh) and 1857(m) cm^{-1} (3)). However one would not expect these peaks to remain constant with time and on increasing the temperature, as the cobalt species are converted into the $Co(CO)_4^-$ complex; however the peak at 1840 was present throughout.

The other species which should be present in solution for the hydroformylation based mechanism are the $HCo(CO)_4$ and $RCOCo(CO)_4$ complexes. These are reported to give infra-red absorptions at :- $HCo(CO)_4$ 2114(w), 2052(m), 2030(s) and 1993(vw) cm^{-1} and $RCOCo(CO)_4$ 2103(m), 2044(s), 2022(s), 2003(vs) and 1720(m) cm^{-1} for $R=C_8H_{17}$ (1). The last peak was not assigned and the author suggested it may actually be due to organic products and not this complex. However this peak is always reported for these species. In both cases evidence in the infra-red exists for the presence of the acyl complex with both hex-1-ene and oleonitrile giving peaks at 2005 and 1710 cm^{-1} as well as the broad absorptions in the 2040 cm^{-1} region. Also in the case of hex-1-ene a peak at 2105(m) was also visible.

(b) <u>$Co(CO)_4^-$/methanol/alkene reaction</u>

In these experiments two different cobalt systems were

studied, firstly the $PPNCo(CO)_4$ complex alone, and secondly a mixture of $PPNCo(CO)_4$ and cobalt (II) acetate. In both cases and for both alkenes, the only peak visible at room temperature was the $Co(CO)_4^-$ peak at 1895 cm^{-1}. On heating the system to 170°C no change was observed and no new carbonyl stretching frequency bands were detected. If the reaction is carried out with ethanol instead of methanol then no change is observed, until the reaction is cooled when two new carbonyl peaks are observed at 2040(m) and 2060(m) cm^{-1}. These are not due to the ethanol solvent and may arise from the acyl species.

5.3. An infra-red study of the methanol/dicobalt octacarbonyl/

alkene system in the presence of petroleum ether solvent

Aim:- to provide a non-polar medium to reduce the disproportionation reaction, and hence observe the effect of higher concentrations of dicobalt octacarbonyl.

5.3.1. Experimental

The conditions used were the same as the above experiment except that the solvent used was a mixture of methanol (2ml) and 80 - 100°C petroleum ether (18ml). As before the reaction was heated in stages with sufficient time allowed for equilibration to occur.

5.3.2. Discussion

In both cases the infra-red initially gave very strong peaks with a broad band centred at 2020 cm^{-1} as well as peaks at 1995(w,sh) and 1855(s) cm^{-1}. In the case of oleonitrile, additional peaks were observed at 1885(m) and 2055(m) cm^{-1}. On heating the peaks above 2000 cm^{-1} weakened and broadened

slightly, at 170°C a broad unresolved band centred at 2005(m) cm^{-1}, and a broad peak at 1740 cm^{-1} became visible. On cooling all the peaks increased in intensity with a new absorption being observed at 2110 cm^{-1}.

The peaks initially present may be assigned to molecular dicobalt octacarbonyl. On heating these peaks become weaker probably due to the reaction of dicobalt octacarbonyl with methanol to give $Co(CO)_4^-$. However this ion normally absorbs at 1895 cm^{-1} but may be shifted due to the non-polar nature of the solvent. The fact that most of the peaks are broad unresolved bands suggests a complex mixture of carbonyl species present in this system, but may also be due to solids suspended in the reaction media. The broad peak at 1740 cm^{-1} and the unresolved band centred at 2005(ms) cm^{-1} together with the peak at 2110 cm^{-1} suggests the presence of the acyl complex (peaks reported at 2103(m), 2044(s), 2022(s), 2003(vs) and 1720(m) cm^{-1} (1)).

5.4. An infra-red study of the methanol/dicobalt octacarbonyl hex-1-ene system with added molecular hydrogen

Aim:- to observed the effect of added molecular hydrogen on the infra-red spectrum.

5.4.1. Experimental

The basic exerimental procedure was the same as that described in section 5.2.1. except that the cell was pressurised to 25 Bar with hydrogen, the pressure then being increased to 160 Bar with carbon monoxide.

5.4.2. Discussion

After one hour at room temperature the only peaks observed

in the infra-red were at 1895(ms) and 2035(m) cm^{-1}. These were

assigned to the $Co(CO)_4^-$ ion and the methanol solvent

respectively. Increasing the temperature had the effect of

decreasing the intensity of the 1895 cm^{-1} peak. By 75°C new

carbonyl peaks were found at 2005(s) and 2105(mw) cm^{-1} as well as

two poorly resolved peaks centred around 2030(m) and 2060(m) cm^{-1}. Increasing the temperature further caused the 1895 cm^{-1} peak

to weaken again with a corresponding increase in the peaks at

around 2000 - 2100 cm^{-1} which broadened. A new broad unresolved

absorption was observed in the 1700 cm^{-1} region. The peaks in the

2000 - 2100 cm^{-1} region are assigned to the acyl complex

$C_6H_{13}COCo(CO)_4$.

This experiment indicates that although initially all the

cobalt may appear to be in the form of the $Co(CO)_4^-$ ion reaction

may occur to generate the acyl species. This according to the

presently believed mechanism, based on the hydroformylation

mechanism, will have occurred via generation of the hydrido

tetracarbonyl cobalt species. If this species was formed it was

not detected. However the peaks due to the $HCo(CO)_4$ complex at

2114(w), 2052(m), 2030(s) and 1993(vw) cm^{-1} may have been

obscured by the acyl complex. Also, due to the polar nature of

the methanol solvent, the hydrido complex is believed to exist

mainly in the form of the $Co(CO)_4^-$ ion resulting from the

following equilibrium

$$MeOH + HCo(CO)_4 \rightleftharpoons MeOH_2^+ + Co(CO)_4^-$$
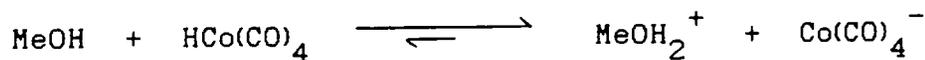
The greater intensity of the acyl peaks in this system compared

to the similar reaction with carbon monoxide alone, presumably

reflects the faster reaction rate for the production of the hydrido complex, in this system the reaction of the acyl species is probably rate limiting.

5.5 The effect of added phosphine ligands on the methanol/ dicobalt octacarbonyl/hex-1-ene system

Aim:- to stabilise any intermediate hydrido and acyl cobalt complexes.

5.5.1. Experimental

The conditions used were the same as those described in section 5.2.1. except that quantities used were dicobalt octacarbonyl (0.3g, 0.9mmol) and triphenylphosphine (0.24g, 0.9mmol).

5.5.2. Discussion

The infra-red spectrum initially showed peaks at 1900(vs) (broad), 2005(sh) and 2020(m) cm^{-1}. On heating these changed: The peak at 1900 cm^{-1} becoming weaker and new peaks occurring at 1955(sh) and 1980 cm^{-1}. These species persisted throughout the remainder of the experiment.

It was hoped that the hydride species $HCo(CO)_3L$ would be evident in this system as this system is far less reactive than the ligand free carbonyl complex. Carbonyl stretching absorptions for $HCo(CO)_3(PPh_3)$ are reported at 2050(mw), 1970(vs) and 1935(w) cm^{-1} (4a) and we assign the peaks at 1980(s) and 1955(w,sh) cm^{-1} to this complex. The initial complex present in solution is $Co(CO)_3(PPh_3)_2^+ Co(CO)_4^-$ which gives peaks at 1900(vs) and 2000 cm^{-1}. On heating, this complex is converted in the reaction possibly to $HCo(CO)_3(PPh_3)$ though this may occur via

$[Co(CO)_3(PPh_3)]_2$ (peaks at 1960(m), 1950(m) and 1902(w) cm^{-1}, the thermolysis product of $Co(CO)_3(PPh_3)_2^+Co(CO)_4^-$ and a complex which will generally separate from solution. Another possible but unlikely intermediate is $Co_2(CO)_7(PPh_3)$ peaks reported at 2079(s), 2026(s), 2010(sh), 1996(m) and 1964(m) cm^{-1} (4b). The data obtained showed no indication of either of these species being present in the reaction mixture.

Conclusion

Infra-red studies of the high pressure carbonylation reaction revealed that before the standard reaction temperature has been reached, a significant proportion of dicobalt octa-carbonyl has been converted into $Co(CO)_4^-$. For systems in which the cobalt species was initially present as the $PPNCo(CO)_4$ salt no other carbonyl species could be detected throughout the experiment. These results support the lower reaction rate found for these systems; as in the faster reaction involving dicobalt octacarbonyl as catalyst precursor there is evidence for the acyl species. This is particularly evident for reactions with added molecular hydrogen. In none of these systems was any evidence found for the existance of the $HCo(CO)_4$ complex in solution. However in systems with added triphenylphosphine evidence was found for the $HCo(CO)_3PPh_3$ species, this is presumably due to the low reactivity of this complex compared to the $HCo(CO)_4$ species towards base abstraction of the proton. But may also reflect the generally lower catalytic activity of phosphine complexes.

Discussion of the alkoxycarbonylation reaction

The general mechanism for the alkoxycarbonylation of

alkenes is thought to be similar to the hydroformylation mechanism proposed by Heck (6). This reaction has received much attention in the past decades (8) and the most satisfactory scheme is shown below:-

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

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

$HCo(CO)_3$ + $CH_2=CH_2$ $\rightleftharpoons$ $HCo(CO)_3$ $\rightleftharpoons$ $CH_3CH_2Co(CO)_3$
$\qquad\qquad\qquad\qquad\qquad\qquad CH_2=CH_2$

3/ $CH_3CH_2Co(CO)_3$ + CO $\rightleftharpoons$ $CH_3CH_2Co(CO)_4$ $\rightleftharpoons$ $CH_3CH_2COCo(CO)_3$

4/ $CH_3CH_2COCo(CO)_3$ + CO $\rightleftharpoons$ $CH_3CH_2COCo(CO)_4$

5/ $CH_3CH_2COCo(CO)_4$ $\begin{array}{c} \xrightarrow{\;HCo(CO)_4\;} CH_3CH_2CHO + Co_2(CO)_7 \\ \xrightarrow{\;H_2\;} CH_3CH_2CHO + HCo(CO)_3 \end{array}$
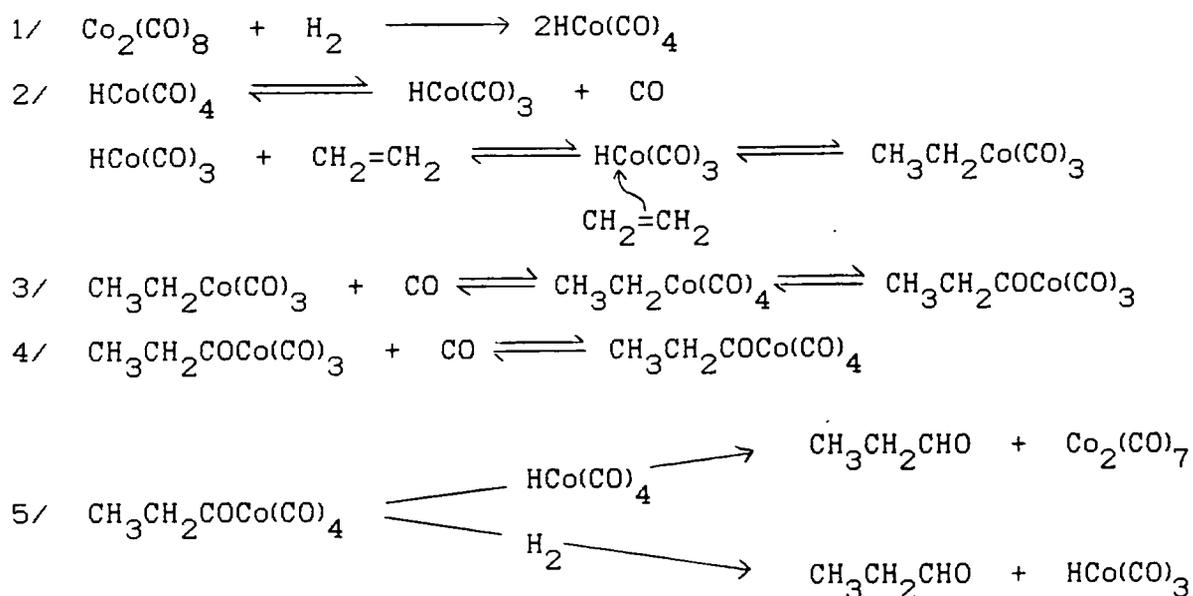
The modifications to this scheme required for the alkoxy-carbonylation reaction are to steps 1 and 5, these are:-

1'/ $Co_2(CO)_8$ + $[H]$ $\rightleftharpoons$ $HCo(CO)_4$

5'/ $CH_3CH_2COCo(CO)_4$ + ROH $\longrightarrow$ CH_3CH_2COOR + $HCo(CO)_4$
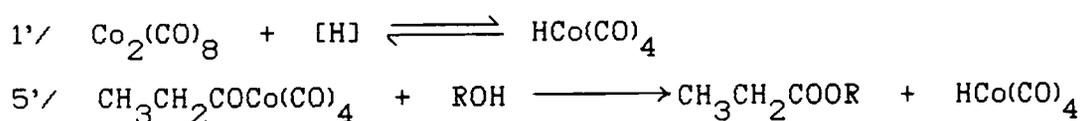
In the following discussion each of these steps will be considered critically as to its importance to the alkoxy-carbonylation reaction; comparisons being made to some other known catalytic systems. This discussion will be followed by consideration of alternative mechanisms and the mechanisms leading to by-product formation.

Step 1 Formation of hydrido tetracarbonyl cobalt (I)

Although the formation of hydrido tetracarbonyl cobalt (I) has been well documented for systems involving mixed carbon monoxide/hydrogen atmospheres (9), its formation in the absence

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of molecular hydrogen is not well understood. It is reported in the literature that a mixture of dicobalt octacarbonyl and ammonia will produce hydrido tetracarbonyl cobalt (I) (10). In the present system three main possibilities exist for the source of hydrogen; these are the alcohol, water impurities and molecular hydrogen impurities. Each of these sources will be discussed in turn.

The first possible hydrogen donor is the alcohol solvent which may react with a cobalt species to produce the hydrido complex. The study of the possible interaction between methanol and dicobalt octacarbonyl is complicated by the facile disproportionation of the dicobalt octacarbonyl by Lewis bases such as methanol (11):-

$$3Co_2(CO)_8 \ + \ 12MeOH \longrightarrow 2Co(MeOH)_6^{2+} \ + \ 4Co(CO)_4^- \ + \ 8CO$$
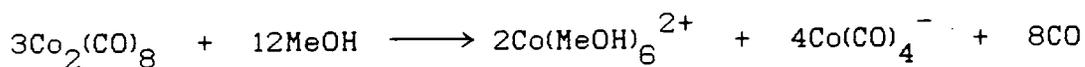
The detection of the disproportionation complex anion suggests that this may be involved directly in the reaction. One mechanism which could include this complex is hydrogen abstraction from an alcohol molecule in the co-ordination sphere of the cobalt (II) ion. Co-ordination of an alcohol to a metal centre polarises the oxygen-hydrogen bond, thus making the hydrogen more acidic and hence easier to abstract. This oxygen-hydrogen bond activation has been quantified by determination of the pK_a values for co-ordinated water molecules to various transition metals (7). Generally the more positively charged the ion the greater the activation.

$$\left[(MeOH)_5 Co \leftarrow :O \underset{\underset{H}{\diagdown} {\delta+}}{\overset{\delta- \diagup Me}{}} \right]^{2+} \rightleftharpoons \left[(MeOH)_5 CoOMe \right]^+ \ + \ H^+$$
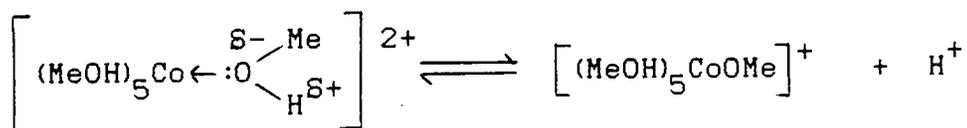
The hydrogen ion thus generated could then interact with the tetracarbonyl cobaltate (-1) ion to give the hydrido species and hence initiate the catalytic cycle. However, our studies have indicated that the tetracarbonyl cobaltate (-1) ion is not an active catalyst. As the presence of tripositive ions, which should be more effective in this activation process, do not increase the activity. Thus this process is thought to be of little importance in this reaction.

A second method for the production of the hydrido tetracarbonyl cobalt (I) species from methanol was proposed by Ercoli and involves the direct reaction between the methanol and a cobalt species (12):-

i.e. $Co_2(CO)_7$ + MeOH $\longrightarrow$ $HCo(CO)_4$ + $MeOCo(CO)_3$

The termination step was then envisaged to be:-

$CH_3CH_2COCo(CO)_3$ + $MeOCo(CO)_3$ $\longrightarrow$ CH_3CH_2COOMe + $1/2Co_4(CO)_{12}$

Ercoli also postulated that the slow step in the reaction is the cleavage of the hydrogen donor. In our study we have found no direct evidence for the existance of $MeOCo(CO)_3$ in the infra-red studies, also it is difficult to explain the effect of bases such as pyridine using this reaction scheme. Although this mechanism cannot be ruled out it is thought to be unlikely.

A second possible hydrogen source is from water impurities in the system either from the solvent, in the gasses used or on the reactor surfaces. Impurities of water could act in the same way as methanol in the above discussion or via the water gas shift reaction:-

$$CO + H_2O \longrightarrow CO_2 + H_2$$
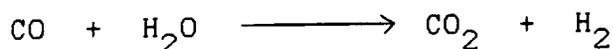
Although cobalt is known to catalyse this reaction the conditions employed are quite severe i.e. 250 Bar and 350-400°C (13). Studies of homogeneous hydroformylation using water as the hydrogen source have made no mention of catalytic activity for dicobalt octacarbonyl (14) although catalytic activity is found for many of the other commonly used transition metals i.e. Fe, Ni, Rh etc. It is interesting to note that iron based systems are more active in the presence of water than with molecular hydrogen as the source of hydrogen for hydroformylation (15). In the equipment used for these reported studies there is exposure of the reactants to iron and other metals present in the reactor walls etc., and their involvement as water gas shift reaction catalysts cannot be ruled out. Studies of hydroxycarbonylation using iron based catalysts have shown poor activity (15); however since iron is an active hydroformylation catalyst with water as the hydrogen source, then it seems likely that in the hydroxycarbonylation reaction that the low activity of iron complexes must be due to slow formation of, or slow reaction of, either acyl or alkyl iron complexes. Hence it is possible in our system that iron, say, acts as a hydrogen source via the water gas shift reaction and the cobalt species performs the remainder of the reaction in preference to iron based species.

The third possible source of hydrogen is hydrogen impurities in the carbon monoxide, this will react directly with any dicobalt octacarbonyl to give the hydrido tetracarbonyl cobalt (I) species. The carbon monoxide used is not totally hydrogen free and contains typically 300vpm of hydrogen. Under

the conditions used in this work this level of impurity will give a cobalt to hydrogen molar ratio of 2:1. The effect of added molecular hydrogen on the rate of reaction is quite significant, a considerable increase in reaction rate was found when even small amounts of hydrogen are added (16). The only complication with postulating direct reaction between dicobalt octacarbonyl and molecular hydrogen is that it relies on there being dicobalt octacarbonyl present to react. In the reaction media the only observable cobalt species before reaction begins is the dissociation complex $[CoL_6]^{2+}[Co(CO)_4^-]_2$. The disproportionation reaction has been claimed to be reversible (17) such that under reaction conditions small quantities of dicobalt octacarbonyl may be formed:-

$$3Co_2(CO)_8 \rightleftharpoons 2Co(MeOH)_6^{2+} + 4Co(CO)_4^- + 8CO$$
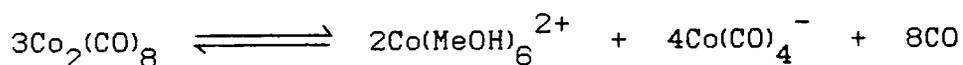
This reversability may also explain why there is an increase in catalytic activity for $PPNCo(CO)_4$ when a cobalt (II) counter ion is added to the system. However the exact nature of the initiation reaction cannot be conclusively ascribed to any one explanation but it seems likely that any hydrogen present will be used to form the hydrido cobalt species.

Step 2 <u>Reaction of hydrido tetracarbonyl cobaltate (I)</u>

<u>with an alkene</u>

Although no evidence was found in the infra-red studies for the existance of the hydrido species it may only be present in small quantities and hence not detectable in the free state. In a similar infra-red study by Whyman using oct-1-ene, no evidence for the presence of the hydrido tetracarbonyl cobaltate was given

(1), again presumably because this species is present only in

very low quantities in the free state. In the alkoxycarbonylation

reaction a further complication exists, namely reaction of the

hydrido tetracarbonyl cobaltate (I) species with the methanol

solvent. As the alcohol is weakly basic and the metal hydride is

sufficiently acidic to be as strong an acid as hydrogen chloride

in methanol (18); then the following equilibrium will lie well

to the right:-

$$MeOH \ + \ HCo(CO)_4 \ \rightleftharpoons \ MeOH_2^+ \ + \ Co(CO)_4^-$$
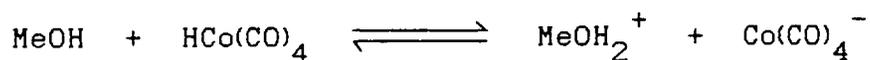
Natta suggested that given the polar reaction media an ionic

mechanism might be involved (19). This would involve

protonation of the olefin followed by interaction of the

carbocation with the tetracarbonyl cobaltate (-1) ion to give an

acyl-like complex and finally an ester:-

$$HCo(CO)_4 \ \rightleftharpoons \ H^+ \ + \ Co(CO)_4^-$$

$$RCH=CH_2 \ + \ H^+ \ \rightleftharpoons \ RCH_2CH_2^+$$

$$RCH_2CH_2^+ \ + \ Co(CO)_4^- \ \longrightarrow \ [RCH_2CH_2 \ [COCo(CO)_3]]$$

$$[RCH_2CH_2 \ [COCo(CO)_3]] \ \longleftrightarrow \ RCH_2CH_2COCo(CO)_3$$

$$RCH_2CH_2COCo(CO)_3 \ + \ CO \ \longrightarrow \ RCH_2CH_2CO^+ \ + \ Co(CO)_4^-$$

$$RCH_2CH_2CO^+ \ + \ R'OH \ \longrightarrow \ RCH_2CH_2COOR'$$
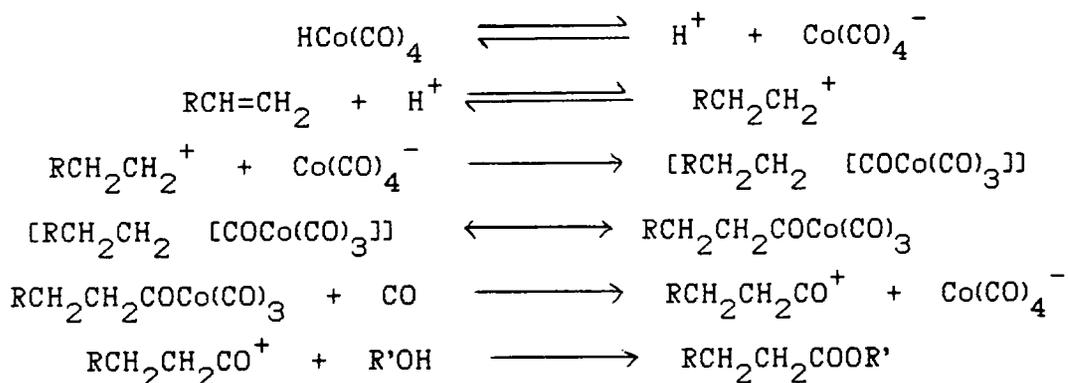
The main disadvantage in applying this totally ionic interaction

is that the initial protonation step will tend to generate

tertiary and secondary carbocations, in preference to primary

carbocations. This would tend to give more branched products

than linear substitution which is not the observed trend. One can

reconcile this conflict if one postulates that the interaction,

between the primary carbocation and the $Co(CO)_4^-$ ion, is

preferred on steric grounds and thus this carbocation will react preferentially. Even if this postulation is valid it is difficult to see how one could generate the degree of isomerisation of the original alkene observed in these reactions in analysis by capillary column g.l.c. of the hex-1-ene systems. Thus it is felt that this mechanism is unlikely to be of major importance.

The reaction shown in step 2 involves the addition of the alkene to an unsaturated hydrido species to give a π-complex; this then rearranges via an insertion reaction to give the alkyl complex. In our infra-red studies no evidence was found for either of these species; however this is not surprising as these complexes are not very stable and are short lived. Generally the only stable alkyl complexes have perfluorinated alkyl groups, owing their stability to the electronegative nature of the perfluoro alkyl group and the fact that β-elimination cannot occur.

$$CF_3CF_2Co(CO)_4 \quad \xrightarrow{\quad\quad\times\quad\quad} \quad CF_2=CF_2 \; + \; FCo(CO)_4$$
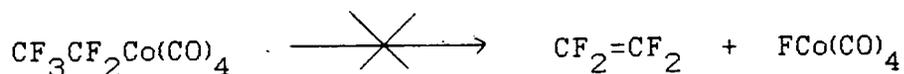
The β-elimination reaction can also be used to explain the large degree of isomerisation of the starting alkene found in these systems, by postulating successive addition/elimination of the hydrido tetracarbonyl cobalt (I) species.

$$RCH_2CH=CH_2 \; + \; HCo(CO)_4 \quad \longrightarrow \quad RCH_2\underset{\underset{Co(CO)_4}{|}}{CHCH_3}$$

$$RCH_2\underset{\underset{Co(CO)_4}{|}}{CHCH_3} \quad \longrightarrow \quad RCH=CHCH_3 \; + \; HCo(CO)_4$$
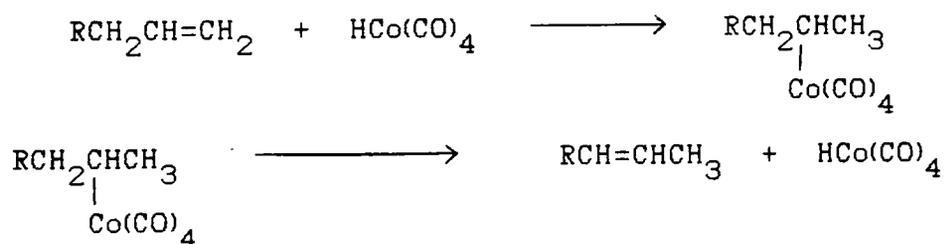
This however cannot be the complete explanation in the case of the hydroformylation reaction, as alkene isomerisation is

found even when the pressures of carbon monoxide used suppress this process. This has been explained by postulating that isomerisation occurs in the initial π-complex (20). Even though the pressures used in our study were in the same region as in the above published work, the high temperatures used make isomerisation by addition /elimination possible in the alkoxy-carbonylation reaction.

Steps 3 and 4 <u>Conversion of the alkyl cobalt species to the</u>

<u>acyl cobalt species</u>

Conversion of the alkyl cobalt tetracarbonyl species is known to be a facile reaction and forms the basis of many synthetic routes to acyl cobalt tetracarbonyl species (21). Our infra-red spectroscopic studies have revealed the presence of acyl tetracarbonyl cobalt (I) species in the alkoxycarbonylation reaction using dicobalt octacarbonyl based catalysts. Conversion of the alkyl compound to the acyl cobalt complex was found to be rapid, such that no carbonyl stretching frequency bands were observed which could be assigned to the alkyl species. Alkyl tetracarbonyl cobaltate (-1) species are only stable at low temperatures and rapidly react above $-35^{\circ}C$.

Step 5 <u>Alcoholysis of the acyl tetracarbonyl cobalt (-1)</u>

<u>complex</u>

The final step in the reaction involves reaction of the acyl tetracarbonyl cobaltate (-1) species with an alcohol to give the ester product and regenerate the hydrido tetracarbonyl cobalt (I) complex. This presumably occurs via nucleophilic attack by the alcohol on the acyl species:-

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$$RR'-\overset{\displaystyle O}{\overset{\|}{C}}-Co(CO)_4 \quad \longrightarrow \quad \left[RR'-\overset{\displaystyle O^-}{\overset{|}{C}}-Co(CO)_4 \right]$$
$$\quad\quad \overset{\curvearrowright}{R"OH} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad R"OH^+$$

$$RR'C\overset{\displaystyle O}{\underset{OR"}{<}} \;+\; H^+ \quad \longleftarrow \quad RR\overset{\displaystyle O}{\underset{OR"}{\overset{+}{<}}} \;+\; Co(CO)_4^-$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad H$$
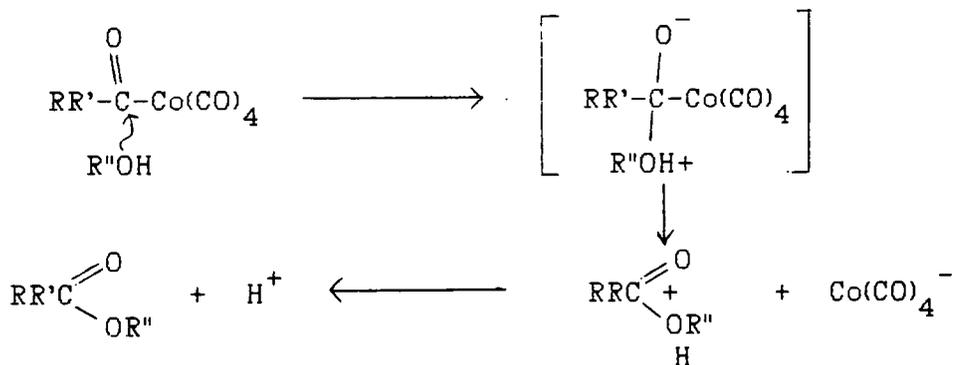
The observation of the existance of the acyl-cobalt complex in the reaction by infra-red spectroscopy would suggest that this alcoholysis is a relatively slow step, and may in fact be rate limiting. The acyl tetracarbonyl cobalt group is a relatively bulky group and thus may make the nucleophilic attack of the alcohol difficult. This effect should be more prominent for the internally substituted esters (i.e. R,R' = alkyl). However the observed degree of branching would tend to suggest that this effect is not very important; as the selectivity toward linear substitution, in the case of hex-1-ene, was not particularly high. A significant degree of steric hindrance should produce large amounts of the linear isomer and only relatively low quantities of branched isomers, this however is not the case. The tetracarbonyl cobaltate (-1) ion is also a relatively weak nucleophile and is a stable species and thus should function as a good leaving group. This group may, however, act as an electron donor and thus reduce the nucleophilicity of the carbonyl group by effecting the electron withdrawing effect of the oxygen atom of the carbonyl group.

The effect of added nitrogen bases such as pyridine on the reaction can be explained if this alcoholysis step is a slow

stage in the reaction. These bases react with acyl compounds to form pyridinium complexes which are more susceptible to nucleophilic attack due to the positive charge on the nitrogen.

$$RR'COCo(CO)_4 \;+\; py \;\longrightarrow\; RR'C\overset{O}{\underset{NC_5H_5}{\diagup\!\!+}} \;+\; Co(CO)_4^{-}$$

$$RR'C\overset{O}{\underset{\overset{+}{N}C_5H_5}{\diagup}} \;+\; R''OH \;\longrightarrow\; RR'C\overset{O}{\underset{OR''}{\diagup}} \;+\; H^{+} \;+\; py$$
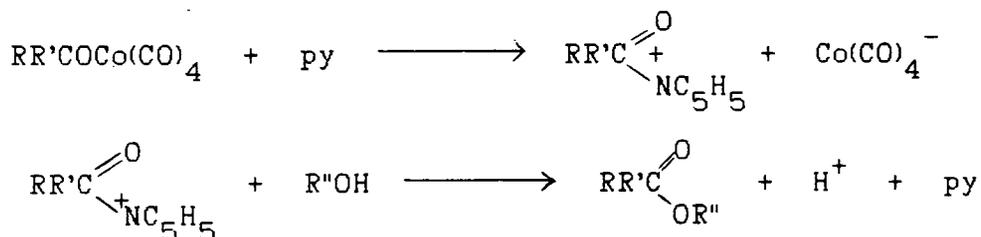
The greater selectivity towards formation of the n-substituted product when pyridine is used, can be explained by the steric hindrance caused by the bulk of this base. The pyridine base will be less likely to form the pyridinium complex for internally substituted acyl-cobalt complexes, and the pyridinium complex formed should be sterically less readily attacked by nucleophiles. Although organic acyl pyridinium complexes are known, no evidence was found for the existance of these species; however; they are presumably relatively unstable as reflected by the increase in reaction rate.

The postulation that alcoholysis of the acyl-cobalt species is a slow step is also supported by the observed order of the reaction with respect to methanol (22). If the final step is rate limiting then a first order reaction, with respect to methanol, would be expected. This is in fact the observed result. Also on the addition of pyridine to the system the order of the reaction, with respect to the alkene, changes from being approximately zero order to being first order. This can be explained if one postulates that the reaction between the alkene and the hydrido-cobalt species becomes the rate limiting step in

the presence of these bases.

Alternative mechanisms

There are few alternative mechanisms that can be envisaged for this reaction; however a number have been postulated. The first is an ionic mechanism proposed by Natta (19), this involves protonation of the alkene by hydrogen ions followed by interaction with the tetracarbonyl cobaltate (-1) ion. The acyl-cobalt complex thus generated would react in a similar way to the scheme proposed above. This mechanism was discussed in step 2 and is thought to be an unlikely alternative.

Evidence for the addition of the $MeCOCo(CO)_4$ complex to the alkene as opposed to the generally excepted $HCo(CO)_4$ complex has been published by Milstein (23). Their reaction scheme is:-

$$Co_2(CO)_8 \ + \ py \ \longrightarrow \ [Co(CO)_4py]^+[Co(CO)_4]^- \ \rightleftharpoons \ Co(py)_6[Co(CO)_4]_2$$

$$Co_2(CO)_4py^+ \ + \ MeOH \ \longrightarrow \ MeOCOCo(CO)_3 \ + \ pyH^+$$

$$MeOCOCo(CO)_3 \ + \ CH_2=CH-CH=CH_2 \ \longrightarrow \ \underset{Co(CO)_3}{\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown}COOMe$$
(I)

$$\underset{Co(CO)_3}{\diagup\!\!\diagdown\!\!\diagup}COOMe \ + \ pyHCo(CO)_4 \longrightarrow \ CH_3CH=CH-CH_2COOMe \ + \ Co_2(CO)_7$$
$$+ \ py$$
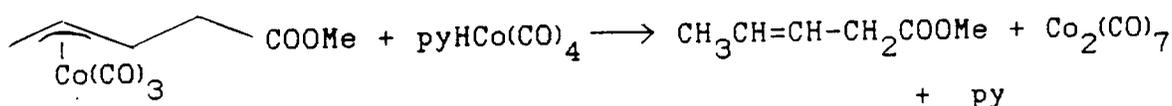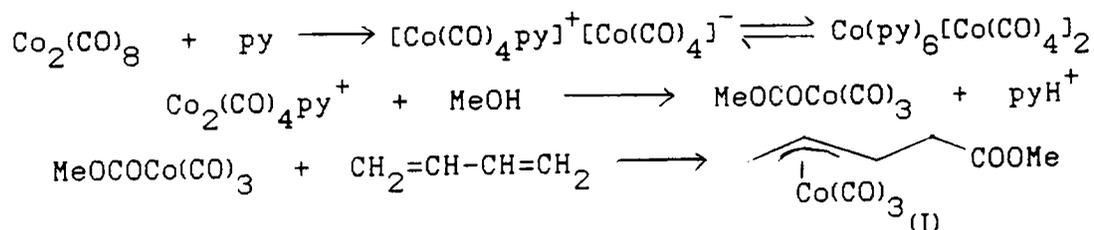
However if this type of mechanism was applied to monoalkenes then intermediate (I) would become:-

$$CH_3CH_2\underset{Co(CO)_3}{CHCH_2}COOMe$$
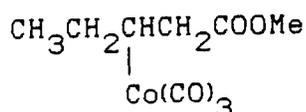
This would not undergo the same termination reaction as detailed above and would instead be expected to generate an acyl species or eliminate the metal hydride. The latter case would give, unsaturated esters and the former would generate a 1,2 disubstituted ester via alcoholysis of the acyl species.

By-product formation

The main by-products observed in this reaction were acetals, formed by reaction of the methanol solvent with aldehydes. However a number of possible side reactions exist which are outlined below:-

1. $2ROH \longrightarrow ROR + H_2O$

2. $RCH_2CH_2OH \longrightarrow RCH=CH_2 + H_2O$

3. $CH_3CH(OH)CH_3 \longrightarrow CH_3COCH_3 + H_2$

4. $H_2O + CO \longrightarrow CO_2 + H_2$

5. $RR'C=CRR' + H_2 \longrightarrow RR'CHCHRR'$

6. $RR'C=CRR' + H_2 + CO \longrightarrow RR'CHRR'CCHO$

7. $2RR'C=CRR' + H_2 + CO \longrightarrow RR'CHCRR'COCRR'CHRR'$

8. $RR'C=CRR' + R''OH \longrightarrow RR'CHRR'COR''$

9. $ROH + CO \longrightarrow RCOOH$
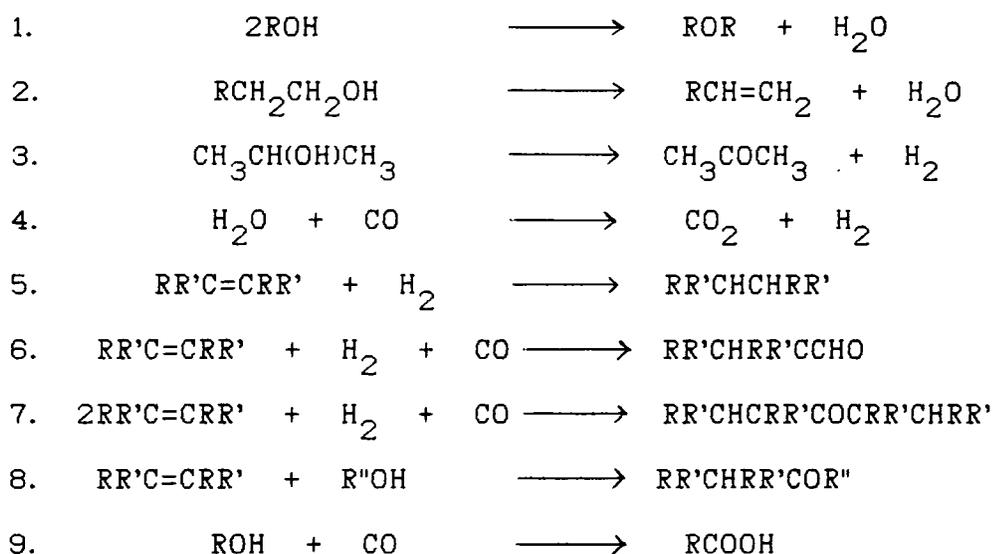
These reactions may be subdivided into two main groups, that is reactions involving the alcohol and those involving the alkene. The reactions involving the alcohol (1-3,9) will be discussed first. Of these reactions only reactions 1 and 9 are applicable to methanol, and indicates the main reason for the choice of this alcohol as co-reactant. In experiments carried out using other alcohols as co-reactants, the yields were noticeably reduced. In the case of t-butanol reduction in yield was quite significant, presumably because of these side reactions. In the case of methanol the product from reaction 1 would be dimethylether, a gas at room temperature (bp. $-25^{\circ}C$) and may have been lost on depressurisation of the reaction mixture. In general the g.l.c. showed little evidence for products derived

general the g.l.c. showed little evidence for products derived from methanol except iodine, methyl iodide and potassium iodide promoted reactions. In these systems reaction 9 is more favourable than in the halide free reactions; which generally require higher temperatures and pressures for carbonylation of methanol to occur. Thus compounds derived from methanol were observed in the g.l.c. but were not characterised. In these systems the reaction scheme could be:-

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

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

$$MeCo(CO)_4 + CO \longrightarrow MeCOCo(CO)_4$$

$$MeCOCo(CO)_4 + MeOH \longrightarrow MeCOOMe + HCo(CO)_4$$

$$MeCOCo(CO)_4 + OH^- \longrightarrow MeCOOH + Co(CO)_4^-$$
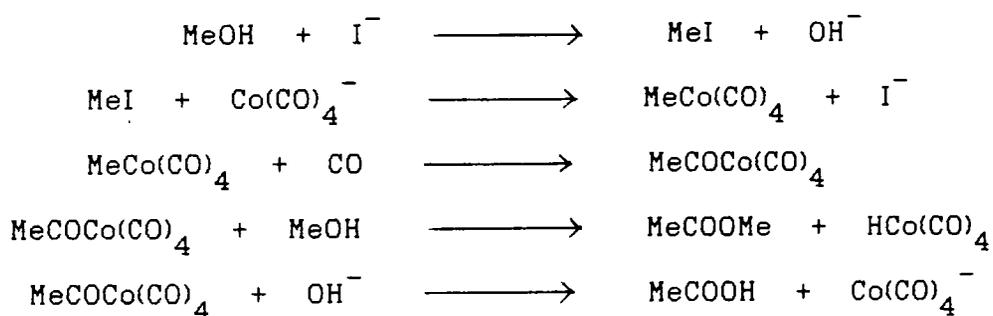
In the case of alkene derived products the only by-product identified in reasonable quantities, was acetal formed from reaction of an aldehyde with the solvent. The aldehydes are formed by reaction 6. in the above list. However it is felt that the hydrogen source is unlikely to be molecular hydrogen as indicated. As mentioned earlier molecular hydrogen has a dramatic effect on the rate of reaction and significant quantities of hydrogen were not present in the system. The other possible source of hydrogen is the hydrido-cobalt complex believed to be involved in the alkoxycarbonylation reaction.

i.e. $Co(CO)_4COR + HCo(CO)_4 \longrightarrow RCHO + Co_2(CO)_7$
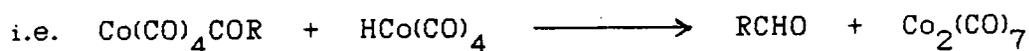
Reduction by molecular hydrogen is believed to occur whist the organic group is attached to the cobalt centre:-

$$\underset{4}{\overset{\displaystyle O}{\overset{\displaystyle \|}{RC}}-Co(CO)} \quad \rightleftharpoons \quad \underset{3}{\overset{\displaystyle O}{\overset{\displaystyle \|}{RC}}-Co(CO)} \; + \; CO$$

$$H_2 \; + \; \underset{3}{\overset{\displaystyle O}{\overset{\displaystyle \|}{RC}}-Co(CO)} \quad \rightleftharpoons \quad \overset{\displaystyle O \;\; H}{\underset{\displaystyle H}{\overset{\displaystyle \| \;\; /}{RC}-\underset{\displaystyle |}{Co}(CO)_3}}$$

$$\overset{\displaystyle O \;\; H}{\underset{\displaystyle H}{\overset{\displaystyle \| \;\; |}{RC}-\underset{\displaystyle |}{Co}(CO)_3}} \quad \longrightarrow \quad RCHO \; + \; HCo(CO)_3$$
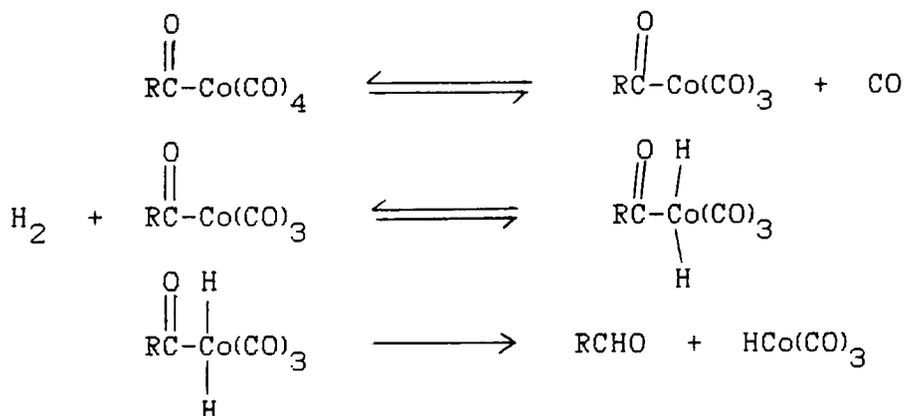
In the homologation of methanol to ethanol the latter hydrogen based reduction is thought to be a more likely reaction mechanism due to the lack of any direct evidence for the existance of hydrido-cobalt species. In the present system these hydrido-cobalt species were again not observed in the reaction mixture by infra-red spectroscopy. However this is not surprising due to the basic nature of the methanol solvent and the high acidity of the hydrido-cobalt complex.

i.e. $\quad HCo(CO)_4 \; + \; MeOH \quad \longrightarrow \quad Co(CO)_4^- \; + \; MeOH_2^+$
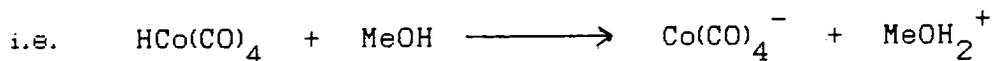
Thus this equilibrium will lie well to the right. Hence at any one time there may only be small quantities of the hydrido-cobalt species in the reaction mixture and thus not be detectable by infra-red spectroscopy. For reduction to involve molecular hydrogen then the reaction must first generate molecular hydrogen as there are only trace quantities introduced as an impurity into the reaction mixture to start with. Both the hydride and molecular hydrogen processes thus seem to be unlikely due to the small quantities of these reagents present in the reaction, of the two it is thought that the hydrogen route is less likely.

The alternative to these two processes not considered so

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far is the direct production of the acetals without formation of the aldehyde. It is, however, difficult to envisage any mechanism which will involve a cobalt complex and generate an acetal product.

Summary

The mechanism generally believed to operate alkoxy-carbonylation reactions implicates $HCo(CO)_4$ as the key species in initiating the catalytic process, by reacting with the alkene to form a metal-alkyl. The rest of the mechanistic schemes parallels the hydroformylation reaction catalysed by cobalt species.

1. $CH_2=CH_2 + HCo(CO)_4 \rightleftharpoons CH_3CH_2Co(CO)_4$

2. $CO + CH_3CH_2Co(CO)_4 \rightleftharpoons CH_3CH_2COCo(CO)_4$

3   $MeOH + CH_3CH_2COCo(CO)_4 \rightleftharpoons CH_3CH_2COOMe + HCo(CO)_4$
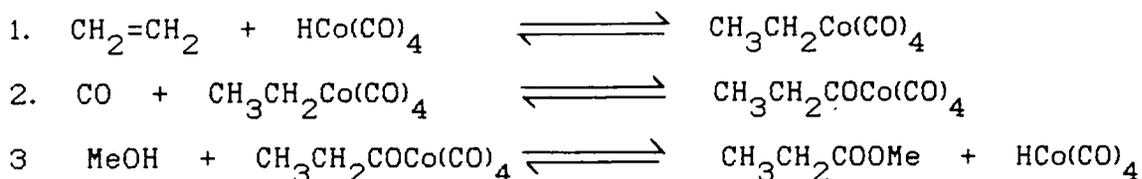
Although the reaction is shown to be composed of three major steps, some of these stages may actually involve a sequence of simpler reactions involving the production of co-ordinatively unsaturated cobalt complexes. For example, step 2. could be considered as occurring in two stages:-

i.e. $CH_3CH_2Co(CO)_4 \rightleftharpoons CH_3CH_2COCo(CO)_3$

$CO + CH_3CH_2COCo(CO)_3 \rightleftharpoons CH_3CH_2COCo(CO)_4$
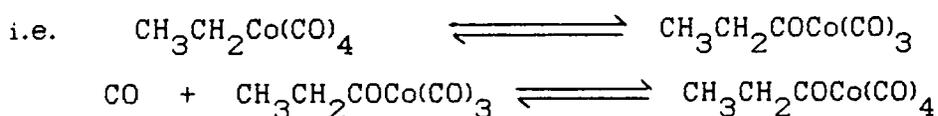
Together with the above catalytic scheme there are two major complicating side reactions, (i) the disproportionation reaction of dicobalt octacarbonyl to form $Co(CO)_4^-$ (ii) the protonation of methanol by hydrido tetracarbonyl cobaltate.

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

(ii) $HCo(CO)_4 + MeOH \rightleftharpoons Co(CO)_4^- + MeOH_2^+$
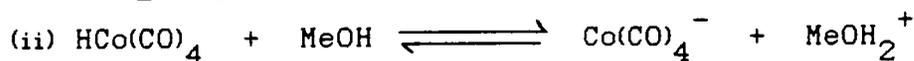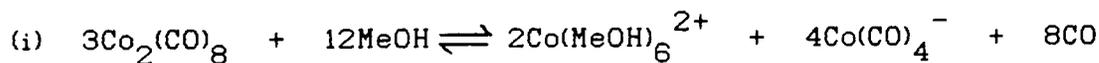
Our studies have shown that the tetracarbonyl cobaltate (-1) ion to be a poor catalyst and as such these reactions serve only to remove cobalt species from the catalytic cycle. High pressure infra-red studies on the reaction indicated that the dominant cobalt species throughout the reaction was the tetracarbonyl

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cobaltate (-1) ion, and no $HCo(CO)_4$ or $Co_2(CO)_8$ were detected except in the very early stages of the reaction. This is in contrast to studies on the hydroformylation reaction (1) which indicated the presence of both of these species at some stage in the reaction.

Although the $Co(CO)_4^-$ ion, with PPN^+ counter ion, is a poor catalyst, the activity of this species can be increased by the addition of a cobalt (II) salt (such as anhydrous cobalt (II) acetate). This activation of the $Co(CO)_4^-$ ion was found to be specific to the cobalt (II) counter ion, other counter ions such as iron (III), chromium (III) and sodium were found to be ineffective. This rules out activation of the alcohol towards hydrogen abstraction, by co-ordination to the positive metal centre, as the mode of action for the cobalt (II) counter ion. One can explain the increased activity of a Co^{-1}/Co^{2+} mixture if the disproportionation reaction is reversible, evidence for which has been given (17). In such a situation cobalt species may be generated which may not necessarily be the fully co-ordinatively saturated dicobalt octacarbonyl complex. If one also postulates the involvement of cobalt carbonyl species other than the $Co(CO)_4^-$ ion, possibly dicobalt octacarbonyl, then this will explain why a mixture of cobalt (II) salts and the $Co(CO)_4^-$ ion is not as effective a catalysts as that derived from dicobalt octacarbonyl. As the reverse of the dissociation reaction is believed to be a slow reaction.

The addition of trialkylphosphines or the addition of halide containing species e.g. MeI, KI, both have the effect of

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reducing the reaction rate. In the case of the trialkylphosphines these ligands react with dicobalt octacarbonyl to give cobalt carbonyl phophine complexes. This prevents the normal disproportionation reaction but the complexes formed are too stable to give any reasonable reaction rates. In the case of halide containing materials the reduced reaction rate may be attributable to two effects, the first being the catalysis of the disproportionation reaction to give CoX_4^{2-} and $Co(CO)_4^{-}$ species. The second effect is the promotion of reactions involving carbonylation of the alcohol to compounds not containing the alkene co-reactant i.e. synthesis of methylethanoate via the $MeCOCo(CO)_4$ complex.

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CHAPTER SIX

AN EXAMINATION OF THE CARBONYLATION

OF N-CHLOROAMINES

6.1. Introduction to the catalytic synthesis of isocyanates and carbamoyl chlorides

The work detailed in the next two chapters is concerned with the catalytic synthesis of isocyanates and carbamoyl chlorides as applied to fatty acid derivatives. Isocyanates and carbamoyl chlorides in many ways have similar chemical properties and it is convenient to discuss then together, highlighting any significant differences between the two. Industrially these materials are very important and find a wide range of use such as in the manufacture of urethane polymers and as amine or alcohol acylating agents in, for instance, the pesticide industry. There is only one widely used organic route to these classes of compounds and involves the use of a highly toxic gas, phosgene. The conditions for the reaction of an amine with phosgene have to be stringently controlled to avoid significant by-product formation, which occurs because the phosgene, with two active chlorine atoms, can undertake disubstitution to form an urea:-

$$RR'NH \xrightarrow{\quad COCl_2 \quad} RR'NCOCl \xrightarrow{\quad RR'NH \quad} RR'NCONRR' + HCl$$
$$+ HCl \qquad\qquad\qquad \text{disubstituted urea as}$$
$$\text{unwanted by-product}$$

The surppression of by-product formation can be achieved by the use of low temperatures with an excess of phosgene present in the reaction mixture. The use of low temperatures (i.e. $0^{\circ}C$ or less) favours the production of the kinetically controlled product, which in this system is the carbamoyl chloride. The thermodynamically preferred product is the disubstituted urea.

The reaction itself is strongly exothermic and thus efficient mixing is required to avoid local hot spots. The presence of an excess of phosgene will also aid the kinetic control of the reaction, but the disadvantage is the need to remove phosgene from the reaction products.

Another disadvantage with the process is the formation of hydrogen chloride, which will readily react with amine in the feed stock to produce amine hydrochloride. This can lead to up to 50% of the amine in the feed stock being converted to amine hydrochloride. As the carbamoyl chlorides of primary amines may undergo elimination of a further mole of hydrogen chloride, thus producing isocyanates, the production of amine hydrochloride may account for more than 50% of the amine input, complete conversion to isocyanates requiring 67% of the feed amine to remove the hydrogen chloride formed.

$$RNH_2 \ + \ COCl_2 \longrightarrow RNHCOCl \longrightarrow RNCO \ + \ 2HCl$$
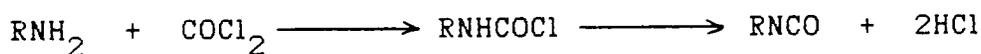
The carbonylation of amines has received much attention in recent years (1,2), many of the reports being in the patent literature (3,4). A variety of carbonylated products can arise from the carbonylation of amines, e.g. formamides, ureas and oxamides.

```
      RNCO                              RR'NCHO
                                      ↗
      R'=H ↖                        ↗
            ↖                      ↗
             ↖        RR'NH       ↗
              ↖    ↗    |    ↘
RR'NCOCONRR' ↙          |      ↘ RR'NCONRR'
                      R"OH
                        ↓
                    RR'NC=O
                         |
                        OR"
```

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Many of the processes occur simultaneously leading to complex mixtures of products. The mechanisms behind many of these transition metal catalysed reactions are similar and may involve carbamoyl complexes formed by nucleophilic attack of an amine on a co-ordinated carbon monoxide ligand.

Transition metal species containing nickel and palladium are known to catalyse many of the above reactions, the products formed depending mainly on reaction conditions and on the type of amine used.

Formation of amides and ureas can be accomplished both catalytically and stoichiometrically, the catalysts used being mainly based upon carbonyl derivatives of manganese, cobalt and nickel. The conditions required are quite severe, typically temperatures in the range 150 - 270°C and carbon monoxide pressures between 100 and 300 Bar being used (5). The products

formed from these reactions depend upon the nature of the amine used; aromatic systems give ureas as the sole or major product (6), whereas aliphatic amines give N-formyl derivatives. In some cases double carbonylation is observed to give oxamides for instance (7):-

$$C_{10}H_{21}NH_2 \xrightarrow[\text{100 Bar,180}^{\circ}\text{C}]{PdCl_2, \text{ 20h}} C_{10}H_{21}NHCONHC_{10}H_{21} + C_{10}H_{21}NHCOCONHC_{10}H_{21}$$
$$(13\%) \qquad\qquad (21\%)$$
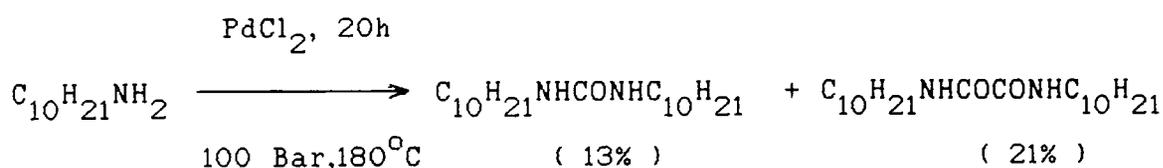
The catalytic formation of isocyanates is less extensively covered in the literature except for one particular class, namely the aromatic isocyanates. The preparation of isocyanates from aromatic nitro compounds has led to a large number of patents as these materials, especially toluene di-isocyanate are industrially very important (8). The process involved requires temperatures of 200°C and pressures of 300 Bar. The mechanism is thought to proceed through nitrene formation via the carbon monoxide assisted rerduction of the nitro-arenes. The nitrene then reacts with carbon monoxide to give an isocyanate.

$$ArNO_2 \xrightarrow{2CO,-2CO_2} Ar\ddot{N}: \xrightarrow{CO} ArNCO$$
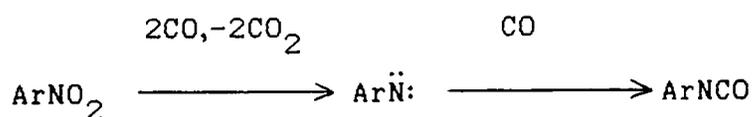
A similar catalytic route involves the use of aromatic amines as starting reagents, and the products are urethanes due to the use of ethanol in the reaction system. A disadvantage of this preparative route is in the use of carbon monoxide/oxygen mixtures, the oxygen being used to reoxidise the palladium metal formed back to palladium (II) (9).

$$\text{PhNH}_2 \ + \ \text{EtOH} \ \xrightarrow[\substack{160^\circ\text{C, 1h} \\ \text{CO/O}_2 \ 85 \ \text{Bar}}]{\text{Pd/C,CsI}} \ \text{PhNHC}\overset{\text{O}}{\underset{\text{OEt}}{\diagup\diagdown}}$$
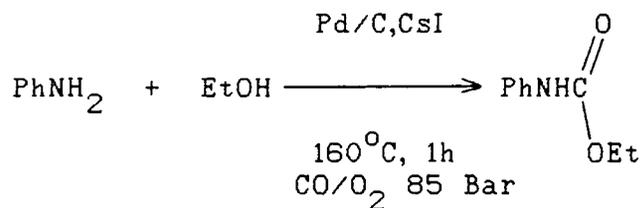
Stoichiometric synthesis of isocyanates can be achieved under relatively mild conditions i.e. 1 - 2 Bar and a temperature of 65 - 85°C (10). The reagent used is a mixture of palladium (II) chloride and disodium hydrogen phosphate. The reaction times are quite long, 21 to 96 hours, and give reasonable yields. The palladium (II) reagent is reduced to palladium metal:-

$$\text{i.e.} \quad \text{RNH}_2 \ + \ \text{CO} \ + \ \text{PdCl}_2 \ \xrightarrow{1 \ \text{Bar} \ 80^\circ\text{C}} \ \text{RNCO} \ + \ \text{Pd} \ + \ \text{HCl}$$
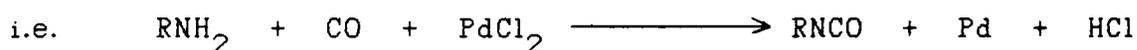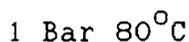
A possible reaction scheme involves conversion of the amine first to a formamide, which then in the presence of palladium (II) chloride is converted into the isocyanate. This mechanism was disproved since under reaction conditions no conversion of formamide to isocyanates was observed. A second possible mechanism involves the production of phosgene from palladium (II) chloride and carbon monoxide. This also was found not to occur as no phosgene could be detected from direct reaction of palladium (II) chloride with carbon monoxide. A reasonable mechanistic route was not, however, proposed by the authors (10).

A second stoichiometric route to isocyanates involves the use of alkene palladium intermediates; again the isocyanate was isolated as a urethane due to the use of methanol as the reaction solvent (11):-

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$$RNH_2 \quad + \quad CO \quad + \quad CH_2\text{==}CH\text{-}CH_2Cl \quad \xrightarrow{PdCl_2} \quad \begin{array}{c} \quad \quad Cl \\ H \quad | \quad CH_2 \\ RN\text{---}Pd\leftarrow\| \\ \quad | \quad CH \\ \quad C \quad | \\ \quad O \quad CH_2Cl \end{array}$$

$$\begin{array}{c} \quad Cl \\ H \quad | \quad CH_2 \\ RN\text{---}Pd\leftarrow\| \\ \quad | \quad CH \\ \quad C \quad | \\ \quad O \quad CH_2Cl \end{array} \quad \xrightarrow[-HCl]{} \quad RNCO \quad + \quad (\pi\text{-allyl } PdCl)_2$$
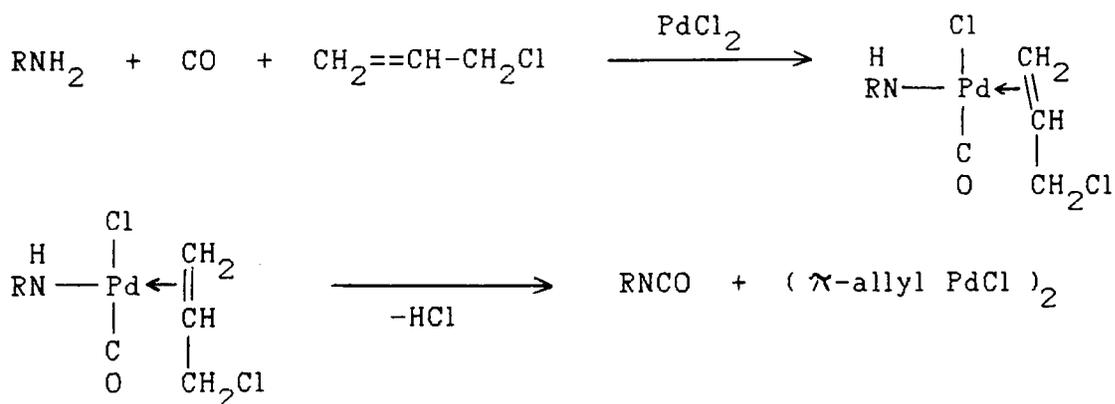
The reaction conditions are mild requiring only the passage of carbon monoxide through the reaction mixture at room temperature. The yield of urethane obtained is 50% after 1 hour with 62% of the palladium present ending up as the π-allyl palladium chloride dimer.

In each of the above transition metal mediated reactions the metal has been reduced or the system required an oxidising agent to be present. This represents one mechanistic route, the other one being the use of a zero bivalent metal species and an "oxidised" substrate. A compound which can be regarded as an "oxidised" amine is an N-haloamine. A stoichiometric synthetic route to ureas has been observed using this type of reactant (12) and nickel tetracarbonyl. The by-product from this reaction was the formation of a small quantity of carbamoyl chloride.

$$RR'NCl \quad + \quad Ni(CO)_4 \quad \longrightarrow \quad \begin{array}{c} RR'N\text{-}Ni(CO)_2 \\ | \\ Cl \end{array} \quad + \quad 2CO$$

$$\begin{array}{c} RR'N\text{-}Ni(CO)_2 \\ \backslash \\ Cl \end{array} \quad \xrightarrow{CO} \quad \begin{array}{c} RR'NCO\text{-}Ni(CO)_2 \\ | \\ Cl \end{array}$$

$$\begin{array}{c} RR'NCO\text{-}Ni(CO)_2 \\ \backslash \\ Cl \end{array} \quad + \quad RR'NCl \quad \longrightarrow \quad RR'NCONRR' \quad + \quad NiCl_2 \quad + \quad 2CO$$

or $RR'NCO\text{-}Ni(CO)_2$ + $RR'N\text{-}Ni(CO)_2$ $\longrightarrow$ $RR'NCONRR'$ + $NiCl_2$
　　　　　|　　　　　　　　　　|　　　　　　　　　　　　　　+ $Ni(CO)_4$
　　　　　Cl　　　　　　　　　Cl
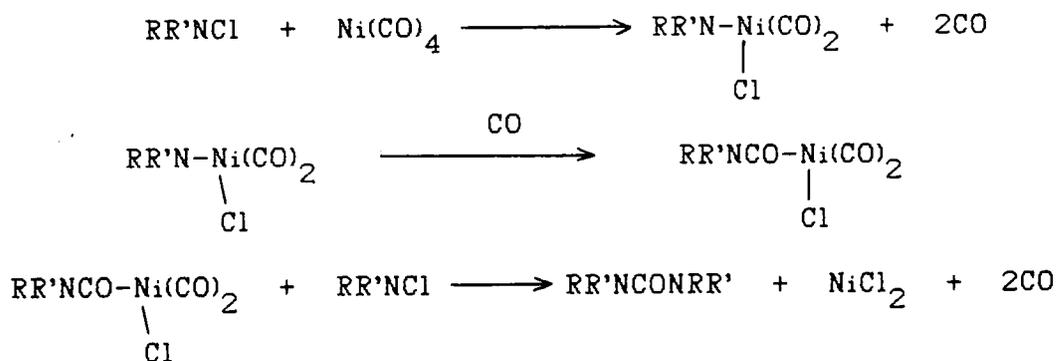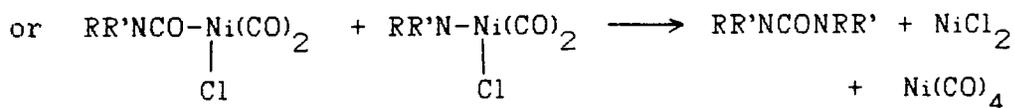
This reaction mechanism was based upon a comparision of the reaction scheme with a more comprehensively studied mechanism for the carbonylation of organic halides. A previous paper by the same authors (13) reported the formation of an anionic carbamoyl nickel complex:-

$$Li^+[Me_2NCONi(CO)_3]^-$$
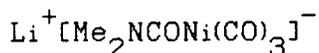
A mechanistically similar, but catalytic, reaction was reported by Saegusa (14) and involved the use of palladium or palladium (II) chloride as catalyst. The reactions were carried out under relatively mild conditions typically $50^{\circ}C$ and 60 Bar pressure of carbon monoxide for 20 hours. The yields were moderate to high (44 to 99%) but the reaction required a large amount of catalyst, typically 1:10 palladium catalyst to N-chloroamine. The catalytic mechanism was not discussed and further work has not been reported on this system.

$$RR'N\text{-}Cl \; + \; CO \; \xrightarrow[\;50 \text{ Bar, } 50^{\circ}C\;]{\text{Pd or } PdCl_2} \; RR'N\text{-}C{\overset{\displaystyle O}{\underset{\displaystyle Cl}{\diagdown}}}$$
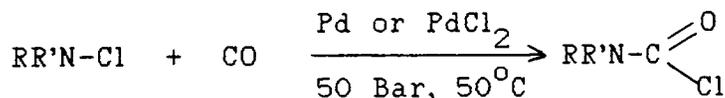
The work described in this thesis concerns a detailed investigation of the above reaction scheme with particular reference to the use of fatty acid amines as reactants. The factors influencing the yield of carbonylated product were studied to gain an insight into the mechanism behind the reaction.

6.2. <u>Reactions between N-chloroamines and carbon monoxide</u>

　　<u>in the presence of palladium chloride and triphenylphosphine</u>

Aims:- to investigate the reactions of N-chloroamines with palladium complexes and to observe the effect of using ligand stabilised palladium catalysts on the production of carbamoyl chlorides.

6.2.1. Experimental

The preparation of N-chloroamines was similar to the method used by Coleman (15). A general example using piperidine, as the amine, is as follows:- To a cold solution of piperidine Hydrochloride (12.2g, 0.1mol) in water (100ml) a cold aqueous solution of sodium hypochlorite (80ml, 0.12mol) was added drop-wise over 15 minutes. After its addition the mixture was stirred for a further 15 minutes and then extracted with diethylether (200ml), which after washing with 8% sulphuric acid and 5% sodium hydroxide solution, was finally dried over anhydrous magnesium sulphate.

The diethylether solution of the N-chloropiperidine was placed into a 600ml Parr autoclave together with palladium (II) acetate (0.224g, 10mmol) and triphenylphosphine (0.52g, 20 mmol). The autoclave was then flushed out several times with carbon monoxide and finally pressurised to 50 Bar carbon monoxide. The system was stirred rapidly and left to react at room temperature for 21 hours. After depressurisation the reaction mixture was filtered to leave a clear yellow solution. The solvent was removed in vacuo and the product distilled at 100°C 12mm Hg to give a colourless liquid. The pipiridyl carbamoyl chloride was identified by comparison (n.m.r. and infra-red) with the authentic compound prepared via direct

phosgenation of the corresponding amine.

6.2.2. Discussion

The results presented in Table 6.1. show that a palladium (II) acetate/triphenylphosphine mixture is an effective catalyst for the carbonylation of N-chloroamines. In the absence of any transition metal species no decrease in the carbon monoxide pressure was observed and the N-chloroamine was recovered in quantitative yield. The addition of a phosphine ligand to the palladium compound enhances the yield in the case of piperidine, from 68 to 81%. In the case of primary amines solvent extraction of the product mixture with chloroform would leave a colourless solid. Elemantal analysis of this reaction product indicates that, in the case of primary amines, hydrochloride salts of the starting amine were present in significant quantities. The carbonylated products were either distilled or converted into ureas by reaction with a suitable amine followed by purification by recrystalisation. The yields of carbonylated products obtained from primary amines were also significantly reduced, as compared to the secondary amines. The use of amines containing oxygen functionalities e.g. morpholine also seems to decrease the catalytic activity of the system giving rise to a lower yield of carbamoyl chloride.

The use of triphenylphosphine in the reaction medium will initially produce palladium phosphine complexes, presumably $Pd(PPh_3)_2(AcO)_2$. Under the reducing conditions of the carbon monoxide atmosphere this may be reduced to the zero valent palladium species i.e. $Pd(CO)_n(PPh_3)_{4-n}$. This reaction is however

Table 6.1.

N-chloroamine	Pressure Bar	Reaction Time hours	Catalyst	Concentration mmol	% Yield
(six-membered ring) N–Cl	50	21	$PdCl_2$	0.1	75
(six-membered ring) N–Cl	50	21	$(PPh_3)_2PdCl_2$	0.1	85
(six-membered ring) N–Cl	50	21	$PdCl_2/PPh_3$	0.1	84
(morpholine ring, O···N–Cl)	50	21	$PdCl_2/PPh_3$	0.2	62
$(CH_3)_3C(CH_3)_2CNHCl$	60	29	$PdCl_2/PPh_3$	0.1	33
$(CH_3)_3CNHCl$	50	21	$PdCl_2/PPh_3$	0.2	37
$(CH_3)_3CNHCl$	65	48	$(PPh_3)_2PdCl_2$	0.1	38
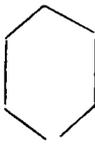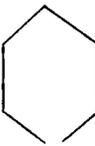
complicated by the fact that the N-chloroamines themselves can react with triphenylphosphine to give yild type complexes (16):-

i.e. PPh_3 + RR'N-Cl $[Ph_3P = NRR']^+Cl^-$

These compounds are relatively stable and are not expected to cause any complications arising from their formation but effectively remove the triphenylphosphine from the reaction medium.

It can be seen from Table 6.1. that the yields obtained from the carbonylation of primary N-chloroamines are only poor to moderate (e.g. 30 - 45%). There are several possible explanations for this observation, perhaps the most obvious reason could be that primary N-chloroamines exhibit a significantly reduced rate of carbonylation. In such a situation the resulting mixture would contain unreacted N-chloroamine as well as carbonylated products. This explanation is, however, not thought to be the case. In the resulting reaction mixtures only trace quantities of unreacted N-chloroamine can be detected. In fact the yield of carbamoyl chloride and the quantity of hydrochloride produced accounted for greater then 90% of the original quantity of amine used in the preparation of the N-chloroamines. Thus it seems likely that the poor yields must be due to the formation of the amine hydrochlorides. There is a possibility that free amine persists from the the production of the N-chloroamine; this is far more likely in the case of the primary amines since an excess of sodium hypochlorite cannot be used in the preparation of the N-chloroamine, to ensure complete

conversion. The reason for not using an excess of sodium

hypochlorite, in the presence of a primary amine, is the

competing side reaction which occurs in such cases to produce

N,N-dichloroamine (17):-

$$RNH_3Cl \quad + \quad NaOCl \quad \longrightarrow \quad RNHCl \quad + \quad NaCl \quad + \quad H_2O$$

$$RNHCl \quad + \quad NaOCl \quad \longrightarrow \quad RNCl_2 \quad + \quad NaOH$$
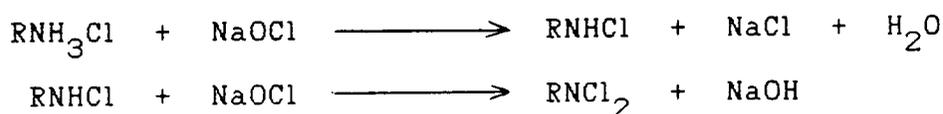
The formation of N,N-dichloroamine can also occur even if

an excess of sodium hypochlorite is not used; this occurs by

preferential chlorination of an N-chloroamine over an

unsubstituted amine. The N-chloroamines are more active than the

parent amine, towards further chlorination. This is due to the

electron withdrawing effect of the first chlorine atom polarising

the nitrogen-chlorine bond, thus making the nitrogen atom more

susceptible towards nucleophilic attack by a hypochlorite ion.

This second chlorination step is, however, kinetically the slower

reaction and thus by suitable choice of reaction conditions

reasonable yields of N-chloroamine can be achieved. The

conditions required are low temperatures and the avoidance of an

excess of the sodium hypochlorite. Even under such restraints the

formation of N,N-dichloroamine cannot be completely ruled out;

production of one molecule of N,N-dichloroamine results in one

molecule of amine remaining unchlorinated and thus leaving free

amine in the N-chloroamine solution. As discussed latter the

N,N-dichloroamines do not undergo carbonylation using the

conditions employed in these experiments; their formation

therefore would lead only to a low conversion to N-chloroamine

and hence to a decrease in the yield of carbonylated products.

A further possibility for the formation of free amine lies in the reaction of N-chloroamines with hydrogen chloride (17), which is formed as a by-product of the carbonylation reaction:-

$$RNHCl + CO \longrightarrow RNHCOCl \longrightarrow RNCO + HCl$$

$$RNHCl + HCl \longrightarrow RNH_2 + Cl_2$$
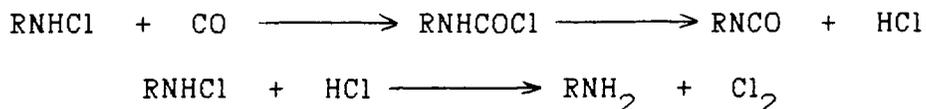
6.3. <u>Reaction of N-chloroamines with carbon monoxide in the presence of various bases</u>

Aim:- to determine the effect of oxygen and nitrogen bases on the yield of carbonylated product and on the formation of amine hydrochloride.

6.3.1. <u>Experimental</u>

The general experimental procedure was as before except that the appropriate base (0.12mol) was added to the reaction mixture in the autoclave. The N-chloroamines used were derived form <u>t</u>-octylamine and <u>t</u>-butylamine. In two cases excess <u>t</u>-octylamine was used in the preparation of the monochloroamine and no additional base was added. In each case any carbonylated products formed were isolated as the corresponding di-substituted ureas by reaction of the crude reaction mixture with an excess of the corresponding amine.

6.3.2. <u>Discussion</u>

The results are presented in Table 6.2. and clearly show that when an organic nitrogen bases are used they completely suppress the reaction. The nature of the nitrogen base used has no effect on the suppression and occurs when relatively small amounts of base are present. This effect may be caused by preferential co-ordination of the amine to the catalytic

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Table 6.2.

N-chloroamine	Base	Yield %
$(CH_3)_3C(CH_3)_2CNHCl$	Et_3N	0
$(CH_3)_3C(CH_3)_2CNHCl$	pyridine	0
$(CH_3)_3C(CH_3)_2CNHCl$	$(CH_3)_3C(CH_3)_2CNH_2$[a]	0
$(CH_3)_3CNHCl$	Et_3N	0
$(CH_3)_3CNHCl$	-	35%
$(CH_3)_3CNHCl$	$NaHCO_3$	36%
$(CH_3)_3C(CH_3)_2CNHCl$		40%
$(CH_3)_3C(CH_3)_2CNHCl$	$KHCO_3$	42%

Conditions:- N-chloroamine 0.1 mole in diethylether (150ml)

Palladium (II) acetate 0.224g, 1.0 mmol

Triphenylphosphine 0.52g, 2.0 mmol

50 Bar carbon monoxide

at room temperature for 18 hours

Base present in excess i.e. 0.13 mole

[a] The base present in this experiment was present in the initial chlorination step i.e. 0.15 mole of t-octylamine was used to prepare 0.1 mole of N-chloro-t-octylamine.

palladium species thus blocking the active sites for the reaction of the N-chloroamine. This may also explain the reduced yield obtained from the carbonylation of N-chloromorpholine, as the oxygen atom present in this amine could function as a σ-donor and hence reduce the activity of the palladium catalyst. Similarly the decrease in yield observed when Saegusa (14) changed the reaction solvent from benzene to 1,2-dimethoxyethane or acetonitrile may arise from such a process. The presence of the inorganic bases has very little affect on the yield of carbonylated products or on the amount of amine hydrochloride formed. This presumably is due, amongst other reasons, to their poor solubility in the reaction medium.

The presence of large quantities of free amine in the initial N-chloroamine solution can therefore be ruled out as product formation is observed. This result is supported by an investigation by g.l.c., of the quantity of free amine left after the reaction between an excess of an amine with sodium hypochlorite. The lower yields found when using primary N-chloroamines may conceivably be due to small quantities of amine left by incomplete reaction. This, as mentioned above, is due to the competing reaction to form N,N-dichloroamine and leave free amine; this, however, would not explain the formation of large quantities of amine hydrochloride. One other complicating factor is the reaction of N-chloroamines with an amine to form a hydrazinium salt (20):-

$$RR'NCl + R''NH_2 \longrightarrow R''NHNRR'.HCl$$

In the systems studied no evidence for hydrazine formation

was found. However, these may have been formed in small quantities and hence not detected.

6.4. Effect of N,N-dichloroamine on the carbonylation reaction

Aim:- to determine the effect of N,N-dichloroamines on the carbonylation reaction.

6.4.1. Experimental

N,N-dichloroamine was prepared by the reaction of t-octylamine (0.2mol) with excess N-chlorosuccinimide (0.25mol) in diethylether at room temperature. The reaction was stirred until no further N-H peak at 3410 cm^{-1} could be observed in the infra-red. The pure N,N-dichloroamine was reacted under similar conditions to the N-chloroamines. A mixture of N-chloroamine and N,N-dichloroamine was also carbonylated in a similar manner.

6.4.2. Discussion

The results obtained indicated that under the conditions employed the N,N-dichloroamine was recovered unreacted, no pressure change was observed and no new carbonyl stretching frequency band was observed in the infra-red. In the case of the mixture of N,N-dichloroamine and N-chloroamine carbonylation of the N-chloroamine was observed. Although the yield of carbonylated material was not determined, due to the potential hazard in isolating N,N-dichloroamines, carbonylation was indicated by the drop in pressure and the presence of a characteristic carbonyl stretching frequency band at 1740 cm^{-1} in the product mixture due to carbamoyl chloride.

The conditions used in these experiments were presumably too mild for any reaction of the N,N-dichloroamine to occur.

N,N-dichloroamines are known to undergo reaction with nickel tetracarbonyl (18) at $20^{\circ}C$ to produce N,N-dialkyl ureas which show a characteristic infra-red carbonyl stretching frequency band at 1660 cm^{-1}. No band at this particular frequency was observed in the palladium catalysed reaction.

It has been reported that there is an equilibrium between N-chloroamine and N,N-dichloroamine (19):-

$$2RNHCl \rightleftharpoons RNCl_2 + RNH_2$$
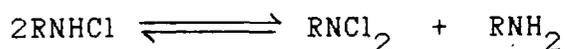
In an experiment in which $\underline{t}$-octylamine was mixed with N,N-dichloro-$\underline{t}$-octylamine at room temperature in diethylether, no N-H stretching frequency band, due to the N-chloroamine at 3260 cm-1, was observed even after several days. Thus if this equilibrium does occur, then the equilibrium constant must lie well to the left hand side in the above equation.

The poisoning effect of free amines in the carbonylation reactions and the fact that carbonylation reactions of N-chloroamines occur up to 81 % yield, indicate that this reaction is of minor importance if it occurs at all.

6.5. The effect of carbon monoxide pressure on the rate
       of reaction

6.5.1. Experimental

The experimental procedure was as described before. A solution of N-chloro-$\underline{t}$-octylamine (0.1mol) in diethylether (100ml) was placed in the autoclave together with palladium acetate (0.224g, 1mmol) and triphenylphosphine (0.52g, 2mmol). The system was then sealed and flushed out several times with carbon monoxide before being pressurised to the required pressure

(7 to 55 Bar). The reaction was then stirred rapidly at room temperature, the pressure of the system being monitored throughout with a piezo sensitive pressure transducer connected to an X-Y chart recorder.

6.5.2. Discussion

The results are presented in Table 6.3. and 6.4.; a plot of logarithm of the pressure verses time is also shown in Figure 6.1. This graph clearly indicates that there is an approximately linear relationship between logarithm of the pressure and time in the initial stages of the reaction (i.e. the first 5 hours). The deviation from linearity in the latter stages of the reaction being caused by a drop in reaction rate as the pressure drops (see later). This is clearly shown by an increase in the half life of the reaction as the pressure drops.

The effect of pressure on the initial rate of reaction is shown in Figure 6.2. The graph indicates that the rate of reaction is strongly dependant on the pressure of the system at low pressure. The further dependency of the rate of carbon monoxide uptake, as the pressure is increased beyond 50 Bar, and hence the reaction rate, appears to become pressure independent as indicated by the leveling off in the rate of carbon monoxide uptake approaching 50 Bar. The limit for the maximum starting pressure was determined by the pressure transducers range, and experiments above 50 Bar were not studied. The dependence of reaction rate with pressures above 50 Bar is expected to be zero order or even inversely dependant. The possible inverse dependency may arise as the large carbon monoxide pressure could

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Table 6.3.

Time h	Pressure Bar	Log_e (pressure)
0	51.0	3.933
1	49.9	3.910
2	48.8	3.888
3	47.5	3.861
4	46.2	3.833
5	44.9	3.803
7	43.0	3.761
10	41.8	3.733
14	40.8	3.708
21	39.6	3.679

Conditions:- N-chloropiperidine (0.1 mol)

$PdCl_2$ (0.885g, 5 mmol)

Benzene (100ml)

Room temperature

Table 6.4.

Pressure Bar	Initial rate of CO uptake at s.t.p $mol/min \times 10^{-5}$
0	0
6.8	2.14
13.6	4.84
27.2	6.18
54.5	7.36
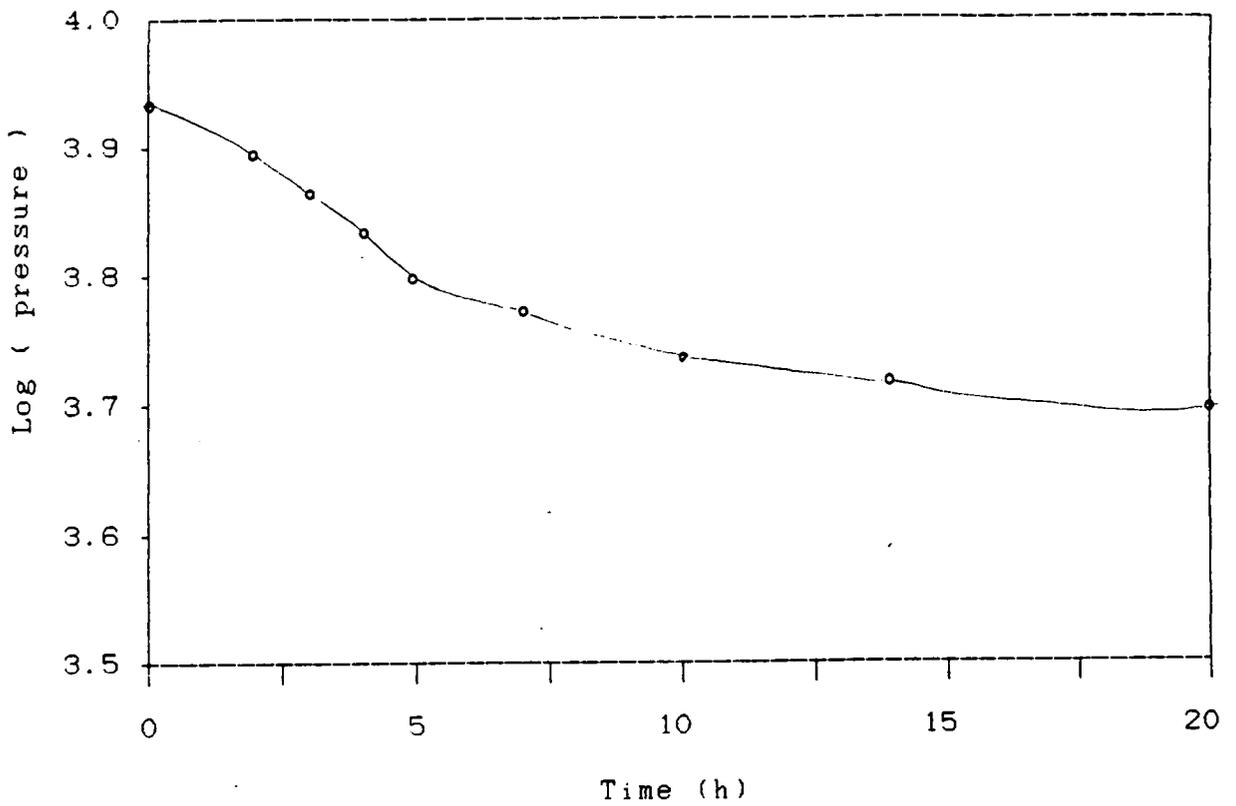
Figure 6.1. Variation of the system pressure with time
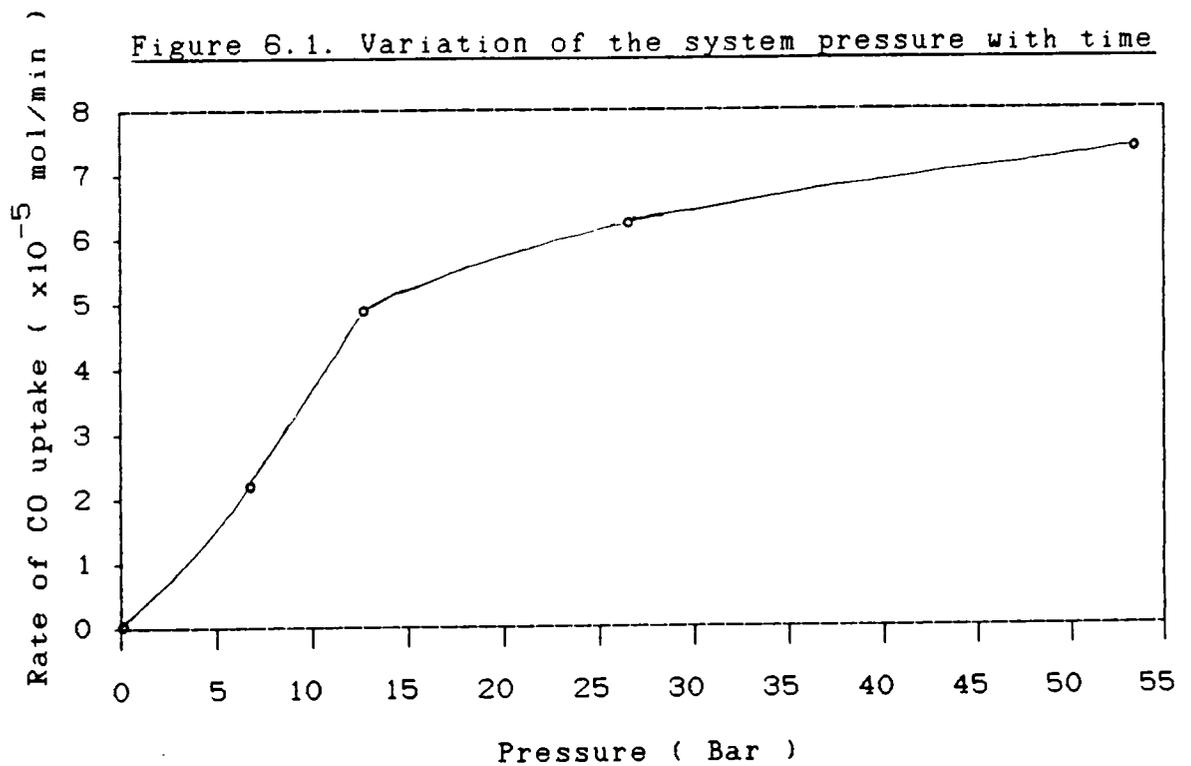
Figure 6.2. Initial rate of carbon monoxide uptake

as a function of initial pressure

stabilise a palladium species and prevent the co-ordination of a reactant molecule.

e.g.
$$PdL_3(CO) \rightleftharpoons PdL_3 + CO$$

$$PdL_3 + RR'NCl \rightleftharpoons PdL_3(RR'NCl) \rightleftharpoons PdL_2(RR'N)Cl + L$$
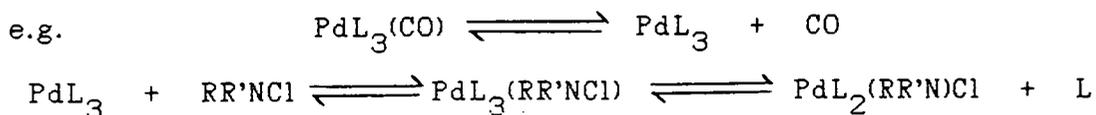
Hence large pressures of carbon monoxide will not favour the dissociation of a co-ordinated carbon monoxide molecule. If however the reaction rate is controlled by a different step not involving carbon monoxide, then there will be little dependence of pressure on the reaction rate.

In a previous study on the methoxycarbonylation reaction the reaction rate was independent of the concentration of alkene used (see section 3.5. Chapter 3). In this system the yield of ester verse time was linear and hence the pressure of the system showed a linear dependence with time. In the present case the reaction does not show a linear dependence for the carbon monoxide pressure, and hence yield of carbamoyl chloride, with time. As in the methoxycarbonylation study the experiment was performed under conditions where the reaction rate is virtually independent of the system pressure. This suggests that the reaction is dependent on the concentration of N-chloroamine, possibly first order from the initial linear dependence of the logarithm of the pressure verses time.

i.e.
$$\underset{+\ PdL_n}{RR'N-Cl} \xrightarrow{slow} Pd(RR'NCl)L_n \xrightarrow[fast]{CO} products$$
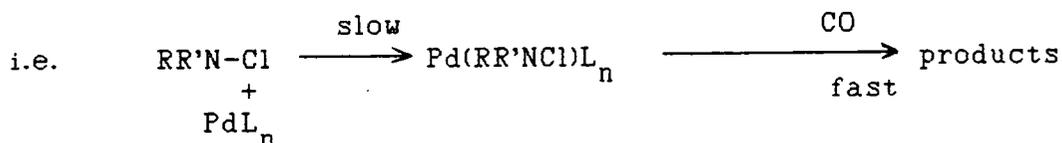
6.6. Effect of the palladium phosphine ratio on reaction

      rate

6.6.1. Experimental

The experimental procedure was similar to that above. N-chloro-t-octylamine (0.1mol) in diethylether (100ml) was placed into the autoclave with palladium acetate (0.224g, 1mmol). The system was flushed out and pressurised to 20 Bar with carbon monoxide. The reaction pressure was then monitored as before.

6.6.2. Discussion

The results are shown in Table 6.5. and plotted graphically in Figure 6.3. The results indicate that the reaction is aided by the addition of a phosphine ligand even in relatively large amounts. It is also quite clear that having an excess of phosphine does not have a detrimental effect on the reaction rate. It might be expected that as the phosphine concentration increases the reaction rate should decrease, this is due to competition for co-ordination sites on the palladium:-

$$PdL_4 \rightleftharpoons PdL_3 + L$$

$$PdL_3 + RR'NCl \rightleftharpoons PdL_3(RR'NCl)$$

(L = CO or PPh_3)
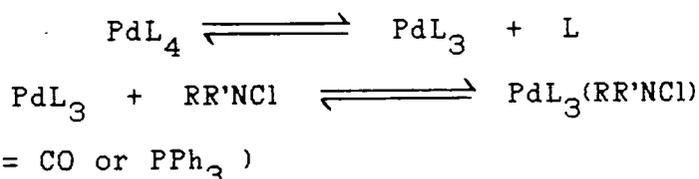
Even though N-chloroamine is present in solution in high concentration it is not as good a ligand as either carbon monoxide or triphenylphosphine. The phosphine ligand is a good σ-donor, whereas carbon monoxide is a good π-acidic ligand. In the case of the N-chloroamines they are less efficient at σ-bonding than amines (not that amines suppress reaction by preferential co-ordination) arising from the electron withdrawing effect of the chlorine atom. This will have the

<u>Table 6.5.</u>

Pd:PPh$_3$	Initial rate of CO uptake at s.t.p. mol/min $\times 10^{-5}$
1:0	2.61
1:1	3.88
1:2	6.62
1:3	5.22
1:4	5.18
1:5	5.04

Moles of PPh$_3$/ Moles of palladium (II)
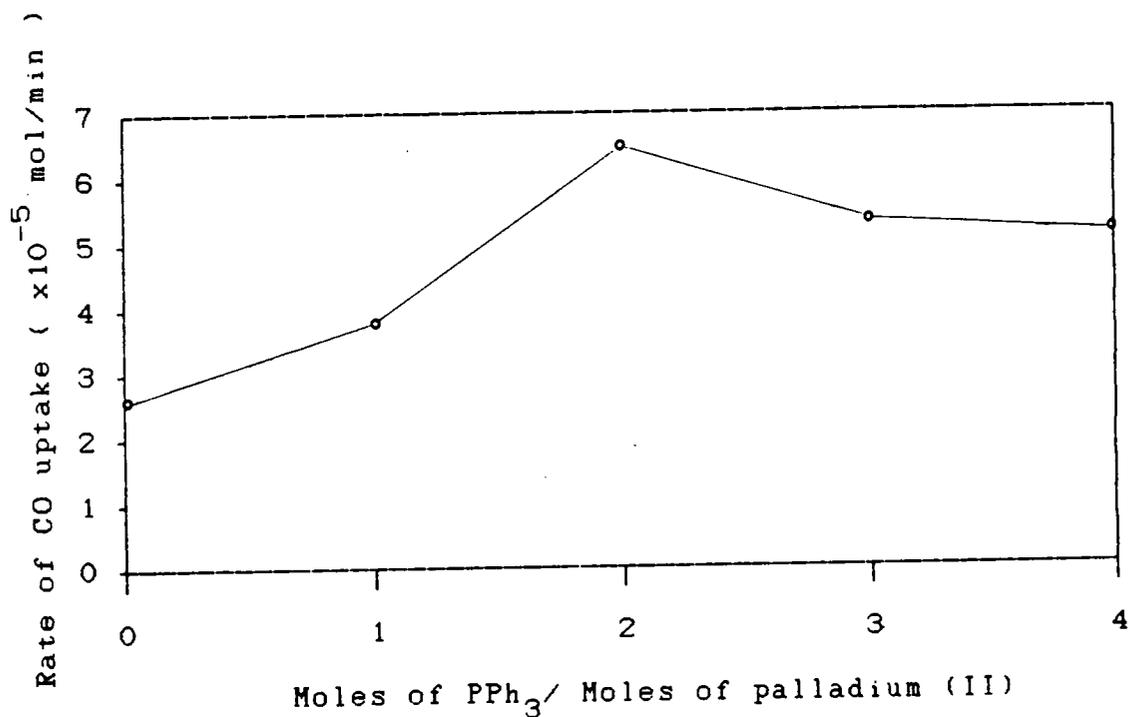
<u>Figure 6.3. Initial rate of carbon monoxide uptake as a function of the P to Pd ratio</u>

effect of reducing the electron density around the nitrogen atom, thus decreasing the availability of the lone pair for σ-bonding. In the case of N,N-dichloroamines the effect will be greater with two electron withdrawing chlorine atoms. Also as the chlorine atom is larger than a hydrogen atom then the N-chloroamine will also be a sterically more demanding ligand and thus less readily co-ordinated than an amine ligand. This effect will be even more prominent in the case of N,N-dichloroamines with two bulky chlorine atoms. Hence the N,N-dichloroamines should not easily co-ordinate to the metal centre and thus not effect the reaction to any significant extent, this was indeed found.

The net result of increasing the phosphine concentration should be the decrease in the availability of co-ordinatively unsaturated species, and so prevent an N-chloroamine from interacting. This study has not found this effect to occur, there are two possible explanations for this. The first is that phosphine ligands are vary labile and the number of co-ordinatively unsaturated sites is not significantly reduced. The concentration of N-chloroamine is far greater than the concentration of phosphine ligand, and hence statistically it stands a far greater chance of collision with a co-ordinatively unsaturated species. The second explanation is that the phosphine ligand reacts with the N-chloroamine to give a ylid type compound (16):-

i.e. $RRN-Cl + PPh_3 \longrightarrow [Ph_3P = NRR]^+Cl^-$
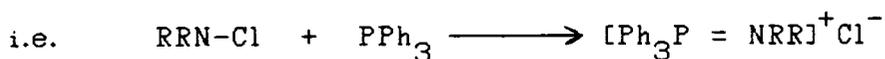
The excess phosphine may thus be removed by the N-chloroamine and not affect the reaction rate. The disadvantage to this

explanation is that the phosphine ligands, on a palladium species, are continually being lost into solution and then replaced, though not necessarily by the same phosphine ligand. These free triphenylphosphine molecules could then react with the N-chloroamine and hence be removed from the catalytic cycle. Thus the added triphenylphosphine should be consumed as the reaction proceeds. The rates of gas uptake however were only recorded in the initial stages of the reaction, where there will possibly be some triphenylphosphine co-ordinated to the palladium catalyst; this is supported by the pale yellow colour of the solution which is typical of palladium phosphine compounds unlike the red/brown colour of palladium acetate solutions.

6.7. Attempted preparation and carbonylation of
N,N-Dichloro-1,6-diaminohexane

Aim:- to produce a di-isocyanate or di-carbamoyl chloride.

6.7.1. Experimental

The 1,6-diaminohexane (11.6g, 0.1mol) was dissolved in cold water (150ml) and hydrochloric acid until the pH was slightly acidic (i.e. 6.5 to 7). This solution was then added drop wise to a cold solution of sodium hypochlorite with rapid stirring. After the addition was complete the product was solvent extracted using diethylether (150ml) and then dried over magnesium sulphate.

The ether solution was carbonylated by placing it into the autoclave with palladium (II) acetate (0.224g, 1 mmol) and triphenyl phosphine (0.52g, 2 mmol). The system was flushed out and pressurised to 50 Bar with carbon monoxide. After 14 hours

stirring at room temperature little carbonylation (as indicated by retention of pressure) was observed. On opening the autoclave a grey/black precipitate was found. Analysis of the mixture was carried out by infra-red spectroscopy and found to be mostly unreacted N-chloroamine, with a small amount of carbonylated material present.

6.7.2. Discussion

The infra-red indicated that no carbonylation had taken place, the spectrum showed that both free amine and mono-chloroamine were present by N-H stretching frequency bands at 3415(s) and 3260(m) cm^{-1} respectively. The carbonylation presumably failed due to the presence of free amine, as discussed in section 6.3., from competition between monochlorination and dichlorination of individual amine groups. As the monochloroamine group is more active towards chlorination than the initial amine group then any monochloroamine initially formed may undergo further chlorination. This effect will be more pronounced towards the latter stages of the reaction, when relatively few free amine groups are left and a large number of monochloro groups are present.

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CHAPTER SEVEN

CARBONYLATION OF FATTY ACID

N-CHLOROAMINES

7.1. Introduction

The work reported in this chapter is concerned with the formation of fatty acid N-chloroamines, their catalytic carbonylation and characterisation of the products obtained. The work also includes further mechanistic studies, and the 'in situ' study of possible catalytic species by high pressure infra-red spectroscopy.

7.2. Preparation of N-chloroamines derived from fatty acid amines.

There are three general routes to N-chloroamines and, as reported in the previous chapter, the most widely applicable route is the reaction of an amine hydrochloride with sodium hypochlorite, at low temperatures (i.e. $<0^{o}C$). This method however cannot be generally applied to fatty acid amines. The primary disadvantage to this method lies in the insolubility of these compounds in cold water. This is especially true for the dialkyl amine hydrochlorides. The second widely used route involves the use of halogenating agents such as N-chloro-succinimide. This method also has its drawbacks; it is relatively slow, requires the removal, if possible, of the succinimide formed, and has the added disadvantage of being an expensive industrial route. The third method involves the use of hypochlorous acid which directly chlorinatiates the fatty amine. The last method was the one chosen as being the most useful and is discussed in more detail.

The use of hypochlorous acid involves the addition of a known quantity of hypochlorous acid to an amine in an organic

solvent, the reaction being cooled, preferably to below 0^oC, as with the hypochlorite route. The requirement that the reaction be carried out at as low a temperature as possible, is difficult to achieve in practice for the fatty amines. This difficulty arises from the poor solubility of these amines in most organic solvents especially at the reaction temperatures required. These amine are only soluble to any practically useful extent in a limited number of solvents, such as chloroform and toluene. Even in these solvents the solubility is considerably reduced at or below 0^oC

As the reaction required the hypochlorous acid to be dissolved in an organic solvent a preliminary series of experiments were conducted to find the most suitable solvents for this purpose. These consisted of the generation of hypochlorous acid, by the reaction of sodium hypochlorite solution and hydrochloric acid, in the presence of the solvent under test. The reaction was performed between -10^oC and 0^oC with vigorous stirring, the hydrochloric acid being added dropwise so as to avoid local heating, due to the exothermic nature of the reaction. The latter also helps to suppress the liberation of chlorine caused by the decomposition of the hypochlorous acid in the presence of a local excess of hydrogen chloride. The mechanism for which is likely to be:-

$$HOCl + HCl \longrightarrow H_2OCl^+ + Cl^- \longrightarrow H_2O + Cl^+$$
$$Cl^+ + Cl^- \longrightarrow Cl_2$$
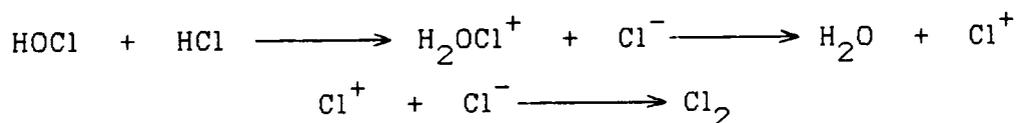
The dropwise addition of concentrated hydrochloric acid was continued until the pH of the aqueous layer was about 6 to 6.5, at which pH virtually all the hypochlorite is in the form of

hypochlorous acid (1). The mixture was then allowed to separate in to phases and the organic layer removed. The remaining aqueous layer was extracted with further portions of the organic solvent, the extracts were combined and dried over anhydrous calcium chloride. The quantity of hypochlorous acid extracted was then determined by iodometric titration of the organic hypochlorous acid solution:-

$$HOCl \; + \; HCl \longrightarrow H_2O \; + \; Cl_2$$

$$Cl_2 \; + \; 2KI \longrightarrow I_2 \; + \; 2KCl$$

$$4H^+ \; + \; I_2 \; + \; 2S_2O_4^{2-} \longrightarrow 2I^- \; + \; S_4O_6^{2-} \; + \; 2H_2O$$
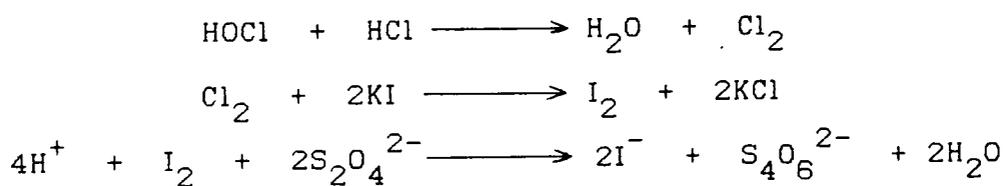
The solvents tried were diethylether, methylethylketone, chloroform and dichloromethane. The results indicated that methylethylketone was the most effective solvent, with about 70 - 80% of the hypochlorite being converted into usable hypochlorous acid. Thus strong solutions of hypochlorous acid, up to about 1.6M, could be made. These solution were stable for several days if kept cold i.e. below $0^{\circ}C$ but decompose slowly possibly involving chlorination of the solvent, they were generally prepared immediatly before use. Regarding the other solvents, the chlorocarbons were not as efficient at extracting the hypochlorous acid, and diethylether presented a serious problem: On several occasions the solution of hypochlorous acid in diethylether underwent a vigorous reaction. The solution became relatively warm and started to boil and liberating the hypochlorous acid in the process. This reaction could not be stopped by cooling of the diethlyether, even to $-20^{\circ}C$. The reaction was not due to peroxide radicals (as prior tests for

peroxide contamination proved no radicals were initially present in the ether) but seemed to have an induction period typical of a radical reaction. It was thus decided that diethylether should not be used as a solvent for this process; however, reasonably strong solutions (>1M) could be made and on a few instances chlorination of an amine was successfully achieved using this medium.

For each solvent studied, the organic phase had a slight green/yellow tinge suggesting that some free chlorine was also present in solution. These solutions could not be obtained without some chlorine contamination and were used without further purification due to practical difficulties in removing the chlorine. Thus the iodometric titrations would over estimate the amount of hypochlorous acid present in the solvent.

As mentioned earlier, the fatty amines are only readily soluble in a few organic solvents; unfortunately methyl-ethylketone was also found to be unsuitable due to poor solubility at low temperatures (i.e. $-10^{\circ}C$). The chlorination of fatty amines was hence carried out by dissolving the amine in chloroform. The solution of hypochlorous acid, which required the use of methylethylketone as solvent, was added to the amine solution in chloroform dropwise, the whole system being cooled to $-10^{\circ}C$. The reaction between an amine and hypochlorous acid is highly exothermic, and thus efficient stirring is required to keep the temperature down to below $0^{\circ}C$.

The resulting solution of N-chloroamine in the mixed methylethylketone/chloroform solvent could, in the case of the

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secondary amines be purified by washing the solution with aqueous solutions of 10% sodium hydroxide followed by 5% sulphuric acid. For the secondary amines the chlorination was carried out with a 5% excess of the hypochlorous acid but if this were used for primary amines the reaction would to dichlorination, to produce N,N-dichloroamine as unwanted by-product. In both cases the N-chloroamine can be isolated by removal of the solvent to give an off-white waxy solid.

The second method used to prepare N-chloroamines involved the use of amine hydrochloride salts, these hydrochloride salts had to be prepared from the amine itself. As the fatty amines are virtually water insoluble, the amine hydrochloride salts were prepared by dissolving the amine in a suitable solvent, usually chloroform, and bubbling hydrogen chloride through the solution. The gelatinous precipitates of the amine hydrochlorides can then be filtered off, washed and dried. The N-chloroamines were then prepared by stirring a mixture of the amine salt, with aqueous sodium hypochlorite solution at room temperature for several days followed by chloroform extraction. The chloroform layer was dried and then used without further purification.

The third method employed involved direct chlorination by N-chlorosuccinimide, facilitated by stirring the amine and the N-chlorosuccinimide in chloroform at room temperature (2) for 24 hours.

e.g.

$$
\begin{array}{c}
H_2C-C=O \\
|\qquad\diagdown \\
\qquad\qquad NCl \;+\; RR'NH \longrightarrow RR'NCl \;+\; \\
|\qquad\diagup \\
H_2C-C=O
\end{array}
\qquad
\begin{array}{c}
H_2C-C=O \\
|\qquad\diagdown \\
\qquad\qquad NH \\
|\qquad\diagup \\
H_2C-C=O
\end{array}
$$
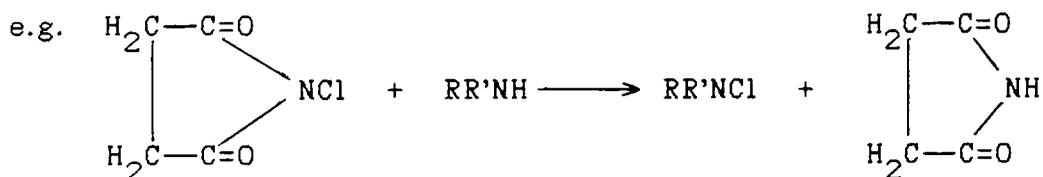
7.3. Carbonylation of the secondary fatty N-chloroamines using a palladium (II) acetate/triphenylphosphine catalyst.

Aim:- to determine the suitability of N-chloro-dialkylamines, prepared by each of the above methods, for conversion to carbamoyl chlorides.

7.3.1. Experimental

A solution of N-chloroamine (0.02mol) was prepared using one of the above methods. In each case the solvent volume was adjusted to 150ml after preparation. The N-chloroamine solution was then placed into the autoclave together with palladium (II) acetate (0.0448g, 0.2mmol) and triphenylphosphine (0.10g, 0.4 mmol). The system was then sealed, flushed out with carbon monoxide, pressurised to 50 bar with carbon monoxide and stirred rapidly at room temperature overnight (total reaction time 14 hours). After depressurisation the product mixture was collected and the solvent removed in vacuo. The crude carbamoyl chloride was then extracted with hot $40^{o}C$-$60^{o}C$ petroleum ether, which selectively dissolved any remaining N-chloroamine and the carbamoyl chloride, to leave any amine hydrochloride salt. The extract was then stripped of the petroleum ether and purified by column chromatography using a 15 - 20 cm column of Kieselgel 60 and eluted with chloroform. This treatment removed any catalyst residue, which adhered to the top of the column. The carbamoyl chloride eluted second from the column, the first elutant having similar r.f. values to the starting N-chloroamine, and was present only in very small quantities. The resultant carbamoyl chloride, after removal of the chloroform, was a pale yellow waxy

solid which melted above 35°C.

Characterisation

The carbamoyl chlorides were characterised by infra-red spectroscopy and elemental analysis. For comparison purposes authentic samples of carbamoyl chlorides were prepared using phosgene and the appropriate amine. This reaction was carried out a low temperatures by the addition, to a toluene solution (12.5% w/w) of phosgene, a solution of the amine. The yields from this method were moderate 40 - 50% the reaction being carried out with a 50% excess of the phosgene solution. In each case the infra-red spectra gave a characteristic peak due to the carbamoyl stretching frequency band at 1735(vs) cm^{-1} arising from the R$_2$NCOCl functionality.

7.3.2. Discussion

As can be seen from Table 7.1., the yields obtained varied from 0% to 75%. In the case of the reaction between N-chloro-succinimide and di(n-hexadecyl)amine 'in situ', the reaction failed to produce any carbonylated product although chlorination did occur (as indicated by the presence of an N-Cl stretching frequency band at about 750 cm^{-1} in the infra-red spectrum). The reaction failed presumably for similar reasons to those discussed in section 6.3.2. namely the presence of free amine. In this case and in the previous examples the catalyst was recovered as a grey powder which was not infra-red active. This indicates that reduction of the palladium had occurred, but that the zero valent catalytic species could not be stabilised under the conditions used.

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<u>Table 7.1.</u>

System	% Yield
Di(n-hexadecyl)NCl/Pd(acetate)$_2$/PPh$_3$	75
Di(COCO)NCl/Pd(acetate)$_2$/PPh$_3$	73
Di(n-octadecyl)NCl/Pd(acetate)$_2$/PPh$_3$	72
Di(n-hexadecyl)NCl[a]/Pd(acetate)$_2$/PPh$_3$	0
Di(n-octadecyl)NCl[a]/Pd(acetate)$_2$/PPh$_3$	0
Di(n-hexadecyl)NCl/PdCl$_2$	68
Di(n-octadecyl)NCl/PdCl$_2$	67
Di(n-hexadecyl)NCl[b]/Pd(acetate)$_2$/PPh$_3$	10
Di(n-hexadecyl)NCl[b]/Pd(acetate)$_2$/PPh$_3$	11

Conditions:- N-chloroamine 0.02 mol

Palladium salt 0.2 mmol

Triphenylphosphine 0.4 mmol

50 Bar, room temperature, 14 hours

[a]N-chloroamine prepared from amine and N-chlorosuccinimide

[b]N-chloroamine prepared from amine hydrochloride and NaOCl sol.

Di(COCO) amine is derived from the cocoa plant and is a mixture of

C_{12}, C_{14} and C_{16} alkyl chains.

Analysis of products

For $(C_{18}H_{37})_2$NCOCl:- requires C 76.04%, H 12.76%, N 2.40% and
Cl 6.07%. Found C 75.2%, H 11.79%, N 2.3% and Cl 5.9%.

For $(C_{16}H_{33})_2$NCOCl:- requires C 75.02%, H 12.59%, N 3.03% and
Cl 6.71%. Found C 76.0%, H 13.42%, N 2.9% and Cl 6.5%.

The yield of carbamoyl chloride from carbonylation of N-chloroamine, prepared via the amine hydrochloride and sodium hypochlorite route was also poor. This indicates that the direct reaction between an insoluble amine hydrochloride salt and aqueous sodium hypochlorite is not very efficient. This reaction is known to give good yields when the amine used is soluble (3). The Hypochlorite ion is known to undergo the following equilibrium (4) :-

$$NaOCl \; + \; H_2O \; \rightleftharpoons \; NaOH \; + \; HOCl$$

However, under the strongly alkaline conditions present in a 1.5M solution of the hypochlorite the equilibrium lies well to the left. Thus there is little free hypochlorous acid present to undertake chlorination. As a consequence it seems likely that unless a one phase reaction between an amine hydrochloride and sodium hypochlorite is possible, then the yield of N-chloroamine and hence carbamoyl chloride will be low.

In the case of carbonylation of N-chloroamines prepared from hypochlorous acid, as a methylethylketone solution, the yield of carbonylated products were good, though the quantities obtained were slightly down on those obtained for the other dialkylamines reported in section 6.2.1. and by Saegusa (5) for piperidine. The reason may be due to several factors one of which may be the presence of free chlorine in the original hypochlorous acid solution, which will affect the yield, by over estimating the amount of hypochlorous acid in solution. The method used to standardise the acid solution would also include this chlorine impurity and hence give an artificially high reading for the

amount of hypochlorous acid present. The second main reason could be the poorer control of temperature during the chlorination step, due to the very exothermic nature of the reaction. The exothermic nature presumably arises in part by protonation of the amine by the acid. Also the poor solubility of the amine at low temperatures which made it practically difficult to maintain the amine in solution.

In each case no differences were observed using amines of different chain lengths. The dicocoamine is derived from the cocoa plant and is a mixture of n-dodecyl, n-tetradecyl and n-hexadecyl alkyl chains. This means that the amine may have two different chain lengths attached to one nitrogen. The yields for this amine were base on a calculated average molecular weight of amine.

7.4. Carbonylation of primary fatty N-chloroamines using palladium (II) acetate /triphenylphosphine catalyst.

Aim :- to determine the effect of different methods for preparing N-chloromonoalkylamines on the yield of carbonylated species.

7.4.1 Experimental

As before a solution of the above N-chloroamine (0.02mol) was prepared using one of the above methods and the resulting solution carbonylated as in section 7.3.1. After depressurisation of the reaction vessel the solution was stripped of the solvent and the residue extracted using hot 40-60°C petroleum ether leaving any amine hydrochloride present behind. The solvent was then replaced by chloroform and the resulting solution refluxed with an excess of aniline for several hours then allowed to cool.

This process was used to convert the isocyanate / carbamoyl chloride mixture into an N-phenyl urea derivative. The crude mixture was washed several times with dilute hydrochloric acid followed by water. This removed any excess aniline as the amine hydrochloride. The chloroform solvent was then removed, and the crude solid mixture again solvent extracted with hot 40 - 60°C petroleum ether to leave an off-white powder, the insoluble urea derivative. The product could be further purified by column chromatography using a short (10 - 15cm) column eluted with chloroform, or by recrystalisation from a 50/50 mixture of chloroform and 40 - 60°C petroleum ether.

Characterisation

The product was characterised by elemental analysis, 300 MHz ^{1}H n.m.r. and infra-red spectroscopy.

e.g. $C_{18}H_{37}NHCONHPh$, mp. 100-101°C

peak centre	group	relative intensity
7.28	Ph	5
6.49	PhN$\underline{H}$-	1
4.86	$C_{18}H_{37}N_H^-$	1
3.22	$C_{17}H_{35}CH_2NH-$	2
1.26	alkyl chain	37

elemental analysis:- C 77.76%, H 12.15% and N 7.22%

$C_{25}H_{44}N_2O$ requires C 77.27%, H 11.41% and N 7.20%

Authentic samples of the ureas were prepared by reaction of phenyl isocyanate and the required amine. Preparation from phosgene as with the dialkyl amines above, was also attempted.

However in this case the yields were found to be poor 10 - 20%. The infra-red also indicated that formation of the disubstituted urea had taken place, by the presence of characteristic N-H and C=O stretching frequency bands at 3210 and 1660 cm^{-1} respectively.

7.4.2. Discussion

The results are shown in Table 7.2. and indicate that only poor to moderate yields are obtained. As with the secondary amines, the yields obtained when the amine hydrochloride was used in the preparation of the N-chloroamine were poor. The reason must again be the poor reaction between sodium hypochlorite and the amine hyrochloride under the conditions employed, giving a low yield of the N-chloroamine.

The yields obtained from N-chloroamines derived from hypochlorous acid, are similar to the yields obtained for other primary amines. Infra-red spectral analysis of the resulting product mixtures show the presence of both isocyanate and carbamoyl chloride. The formation of isocyanate means that again hydrogen chloride has been formed via elimination from the carbamoyl chloride.

i.e.   RNHCOCl $\longrightarrow$ RN=C=O + HCl
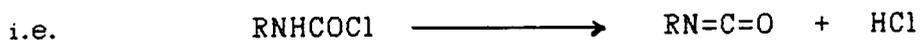
The lower yields obtained for primary amines must be in part due to this acid production, because formation of hydrogen chloride is always accompanied by amine hydrochloride formation. Another contributary effect may be the poor electron donating ability of hydrogen. In the case of dialkyl amines the two alkyl groups can offset the electron withdrawing effect of the chlorine

Table 7.2.

System	% Yield
(n-dodecyl)NHCl/Pd(acetate)$_2$/PPh$_3$	35
(n-hexadecyl)NHCl/Pd(acetate)$_2$/PPh$_3$	37
(n-octadecyl)NHCl/Pd(acetate)$_2$/PPh$_3$	35
(n-dodecyl)NHCl/PdCl$_2$	33
(n-hexadecyl)NHCl/PdCl$_2$	32
(n-octadecyl)NHCl/PdCl$_2$	30
(n-hexadecyl)NHCl[a]/Pd(acetate)$_2$/PPh$_3$	trace
(n-hexadecyl)NHCl[b]/Pd(acetate)$_2$/PPh$_3$	32

Conditions:- N-chloroamine 0.02 mol

Palladium salt 0.2 mmol

Triphenylphosphine 0.4 mmol

50 Bar, room temperature, 14 hours

[a] N-chloroamine prepared from amine hydrochloride and NaOCl sol.

[b] N-chloroamine prepared from amine and N-chlorosuccinimide

atom. With primary amines however, there is only one alkyl group

to offset the electron withdrawing effect. Thus the N-chloro-

amines with one alkyl group should be poorer o-donors than the

secondary N-chloroamines, and hence should co-ordinate much less

readily. If co-ordination of the amine to a metal containing

species is a slow rate determining step, then the yield measured

after a set length of time will reflect the different co-

ordination properties of these ligands.

i.e. $\quad PdL_n + RR'N-Cl \rightleftharpoons PdL_m(RR'N-Cl)$
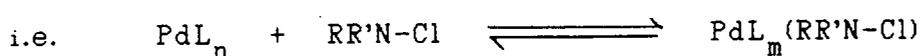
In the case of primary amines (i.e. R' = H) the equilibrium

should lie more to the left compared to the case when a secondary

amine is used (i.e. R,R' = alkyl).

7.5. Reaction between tris(triphenylphosphine) palladium carbonyl and N-chlorodialkylamines.

Aim:- to prepare complexes which may be involved in the catalytic

reaction.

7.5.1. Experimental

Tris(triphenylphosphine)palladium carbonyl was prepared

by standard methods (6); this involved the heating of a

solution of an excess of triphenylphosphine with palladium (II)

acetate in methanol. The reaction being carried out under a

carbon monoxide atmosphere. A chloroform solution of N-chlorodi-

ethylamine was prepared from diethylammonium chloride and sodium

hypochlorite, followed by solvent extraction and purification by

washing with dilute sulphuric acid and dilute sodium hydroxide

solutions. The N-chloroamine solution was then dried over calcium

chloride before being degassed by freeze thaw cycles. N-chloro-

amine (0.01mol) in chloroform (5ml) was then syringed into the palladium carbonyl solution, against a counter current of dry nitrogen. The resulting solution was then stirred at room temperature, the reaction being followed by infra-red spectroscopy. After 24 hours the solution was reduced to dryness under vacuum, then the pale yellow residue was washed with diethylether (10ml) and hexane (20ml) before finally being pumped dry 'in vacuo'. Elemental analysis of the solid gave Pd 16.0%, P 8.25%, Cl 10.4%, C 63.1% and H 6.2%. $Pd(PPh_3)_2Cl_2$ requires Pd 15.1%, P 8.84%, Cl 10.1%, C 61.6% and H 4.3%.

The infra-red spectrum (nujol mull) indicated that no carbonyl stretching frequency bands were present and the spectrum was identical to an authentic sample of $Pd(PPh_3)_2Cl_2$. The solid was also found to be air and moisture stable, as no change in the infra-red was observed after exposure to the atmosphere.

7.5.2. Discussion

No organic product was detected; however since the quantity of starting material was small it is possible that such a product may not be detectable by the methods employed. The formation of a palladium (II) species form a zero valent compound indicates that the N-chloroamines are behaving as oxidising agents. Throughout the experiment no new peaks were observed in the infra-red spectrum; the only change being noted was the disappearance of the carbonyl stretching frequency band at 1955 cm^{-1}, which occurred soon after the addition of the N-chlorodiethylamine. Similar results were found in the reaction between N-chlorodi-ethylamine and other transition metal carbonyl complexes; for

example in the reaction of N-chlorodiethylamine with dicobalt octacarbonyl a rapid evolution of gas was observed which was complete after 15 minutes. During this period there was a rapid decrease in the intensity of the carbonyl stretching frequency bands in the infra-red spectrum, with no new bands being observed. The cobalt finally ending up as solvated cobalt (II) chloride.

The results obtained are qualitatively similar to those of Ryang et al (7) in their work with nickel tetracarbonyl and N-chloroamines. A similar reaction pathway could be occurring in the present system:-

$$Pd(CO)(PPh_3)_3 \longrightarrow Pd(CO)L_2 + L$$

$$Pd(CO)L_2 + RR'NCl \longrightarrow RR'N{:}{\rightarrow}Pd(CO)L_2$$
$$\backslash$$
$$Cl$$

$$RR'N{:}{\rightarrow}Pd(CO)L_2 \longrightarrow RR'N{:}{-}{-}Pd(CO)L + L$$
$$| \qquad\qquad\qquad\qquad\qquad /$$
$$Cl \qquad\qquad\qquad\qquad\qquad Cl$$

$$RR'N{:}{-}{-}Pd(CO)L + L \longrightarrow RR'NCOPdL_2$$
$$| \qquad\qquad\qquad\qquad\qquad /$$
$$Cl \qquad\qquad\qquad\qquad\qquad Cl$$

$$(L= CO, PPh_3)$$

Carboxamide complexes of the type shown are known for palladium, these are air and moisture stable except for ligands with R' = H (i.e. primary amines) which show some decomposition on standing. In the present case these compounds were presumably not isolated due to the presence of an excess of the N-chloro-amine, which as in the nickel case, may undergo further reaction to give organic products.

$$RR'NCOPd(Cl)L_2 + RR'NCl \longrightarrow PdL_2Cl_2 + RR'NCONRR'$$

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Palladium carboxamide complexes were originally prepared by direct reaction of palladium bis(triphenylphosphine) dichloride with an amine under a carbon monoxide atmosphere (8):-

$$Pd(PPh_3)_2Cl_2 \ + \ 2RR'NH \ \xrightarrow[0^{O}C]{CO} \ Pd(PPh_3)_2(CONRR')Cl \ + \ RR'NH_2Cl$$
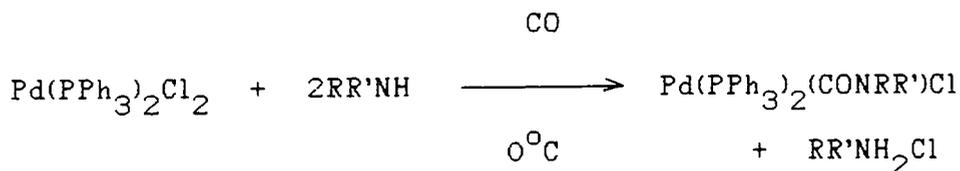
A second method of preparation, employed by Angelici et al (8), involved the use of dialkylcarbamoyl chlorides and a zero valent platinum or palladium species e.g. $Pt(PPh_3)_4$. In this reaction the major proportion of the metal ended up in the form of the bis(triphenylphosphine) dichloride complex. These could have been formed via decarbonylation of the intermediate carbox-amide complex to form an N-chloroamine, followed by a similar reaction to that observed in this work. Two other possible reaction schemes can also be envisaged: The first is oxamide formation:-

$$L_2PdCONRR' \ + \ RR'NCOCl \ \longrightarrow \ L_2PdCl_2 \ + \ RR'NCOCONRR'$$
$$\overset{|}{\underset{Cl}{}}$$
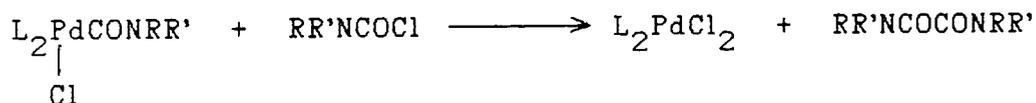
The second possibility is hydrazine synthesis via decarbonylation of the carboxamide complex and subsequent reaction of the amide complex:-

$$2L_2PdNRR' \ \longrightarrow \ L_2PdCl_2 \ + \ RR'N-NRR' \ + \ PdL_2$$
$$(\ L = CO, \ PPh_3 \ )$$
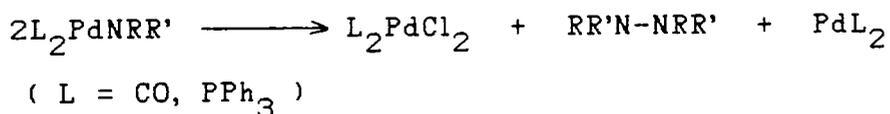
The formation of carboxamide palladium complexes in the reaction would also explain the poor yields obtained from primary amines, as these species are unstable in acidic solutions with acids whose pK_a is less than three (8):-

$$L_2Pd(Cl)CONRR' + 2HX \longrightarrow [L_2Pd(Cl)CO]X + RR'NH_2X$$
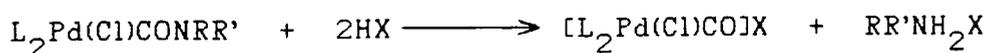
This reaction is very fast and thus explains why sodium hydrogencarbonate and potassium hydrogencarbonate had no effect on the yields obtained. Both of these inorganic bases are insoluble in the reaction media and hence any reaction between hydrogen chloride and the solid base is likely to be too slow to prevent the rapid decomposition of the carboxamide complex. The requirement that acids should have a pK_a of less than three, to cause decomposition, means that ethanoic acid could be present in the reaction mixture. Thus it is conceivable that sodium acetate may function as a suitable base if a solvent could be found in which it is sufficiently soluble.

7.6. An in-situ examination of the carbonylation of N-chloroamines by infra-red spectroscopy.

7.6.1. Experimental

The infra-red cell used was the same as the one detailed in the methoxycarbonylation study and is shown in Figure 2.1. (Chapter 2). The examination involved the study of three palladium catalysts, namely palladium metal, palladium (II) chloride and bis(triphenylphosphine) palladium dichloride. The infra-red spectra were recorded in the region $2500 - 1400 \text{ cm}^{-1}$. The N-chloroamine used was N-chlorodimethylamine, which was prepared by reaction of dimethylammonium chloride with sodium hypochlorite at $0^{\circ}C$. The N-chloroamine was solvent extracted with chloroform and reactions were carried out in this medium. Each of the catalysts used will be discussed in detail.

(a) Palladium metal

Palladium metal was freshly prepared by reduction of an aqueous solution of palladium chloride with hydrazine hydrate, the solid was filtered off, washed with methanol and then dried in vacuo. The palladium metal (0.1g, 1.0mmol) was placed into the infra-red cell with N-chlorodimethylamine (0.05mol) in chloroform. The system was flushed out with nitrogen and pressurised to 65 Bar with carbon monoxide. The solution was heated to 50°C and monitored in the $1600 - 2000$ cm^{-1} region. The infra-red initially showed no carbonyl stretching frequency bands, but on heating peaks appeared at 1680(s), 1715(s) and 1755(m) cm^{-1}. After 15 minutes no further changes to these peaks occurred, but two new carbonyl peaks were observed at 2100(m) and 2160(m) cm^{-1}. These remained throughout the experiment with the peak at $1715 cm^{-1}$ strengthening. On cooling the peaks remained unchanged, but after depressurisation the peaks at 2100 and 2160 cm^{-1} disappeared.

(b) Palladium (II) chloride

Palladium (II) chloride (0.9g, 5mmol) and N-chlorodimethylamine (0.05mol) were placed in the autoclave. The system was flushed out with nitrogen, pressurised to 65 Bar, and heated to 50°C. Initially at room temperature no carbonyl stretching frequency bands were observed but on reaching 50°C a peak was found at 2140(s) cm^{-1}. After 15 minutes at 50°C a broad peak at 1680(s) cm^{-1} with an unresolved shoulder at approximately 1760(s) cm^{-1} were detected. These peaks remained unchanged on increasing the pressure to 100 Bar, and did not change with time. After

cooling and depressurisation the peak at 2140 cm^{-1} disappeared but the peaks at 1680 -1760 cm^{-1} remained constant.

(c) Bis(triphenylphosphine) palladium dichloride

As before bis(triphenylphosphine) palladium dichloride (1.0g, 1.4mmol), with N-chlorodimethylamine (0.05mol) in chloroform were placed in the autoclave which was flushed with nitrogen, pressurised to 65 Bar with carbon monoxide and agitated at room temperature. Following pressurisation carbonyl stretching frequency peaks appeared at 2120(m), 1755(w) and 1670(w) cm^{-1}. After 15 minutes these peaks remained but their intensities had changed. The peaks at 1755 and 1670 cm^{-1} became stronger and the peak at 2120 cm^{-1} weakened; a new peak at 1715 (w,sh) cm^{-1} was also observed. After another 15 minutes the three peaks at 1670, 1715 and 1755 coaleased and their intensities increased greatly. On elevating the pressure to 100 Bar no change in the peaks at around 1700 cm^{-1} was observed, but the peak at 2110 cm^{-1} changed its intensity from weak to medium. No further change was observed on standing. After depressurisation the peaks at 2100 cm^{-1} disappeared, but the peaks at 1670, 1715 and 1755 cm^{-1} remained.

7.6.2. Discussion

An authentic sample of dimethyl carbamoyl chloride in chloroform gives one carbonyl stretching frequency band at 1725 cm^{-1}. It is clear from the above results that formation of the carbamoyl chloride occurs in the early stages of the reaction; no induction period was noted. The results also indicate that the rate of reaction probably increases with increasing temperature, this conclusion being based on the strength of the carbonyl

stretching frequency band at 1715 cm^{-1} which increased in the early stages of the reaction. It is also clear from the study that the carbonyl stretching frequency bands observed are independent of the palladium species used to catalyse the reaction. These bands must be due to palladium carbonyl species present in solution, except for the 1715 cm^{-1} peak which is assigned to the carbamoyl chloride. The remaining two peaks cannot, in the case of the triphenylphosphine stabilised reaction, be assigned to the carbamoyl complex (PPh$_3$)$_2$Pd(R$_2$NCO)(Cl) isolated by Angelici (8), as this species has a carbonyl stretching frequency band at 1610 cm^{-1}. These peaks also cannot be assigned to organic nitrogen containing species as most carbonyl compounds with an adjacent nitrogen atom give rise to carbonyl stretching frequency bands in the region of 1660 cm^{-1}, for example the ureas formed in the characterisation of the carbamoyl chlorides give peaks at 1660 cm^{-1} in their infra-red spectra. The reason for the low carbonyl stretching frequency is due to the interaction of the nitrogen lone pair with the π-system of the carbonyl group, i.e. the following canonical structures can be envisaged:-
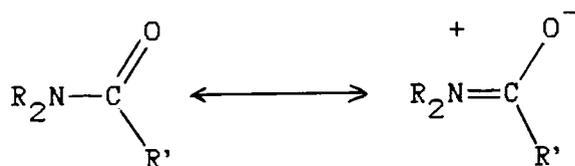
This effect can also be seen in the carboxamide complexes, as these compounds give carbonyl stretching frequency bands at lower frequencies than their non-nitrogen containing analogues. In the case of the carboxamide complexes a further canonical

structure can also be envisaged:-

$$R_2N\overset{+}{=}\overset{\overset{\displaystyle O^-}{|}}{C}-PdL_n \longleftrightarrow R_2N-\overset{\overset{\displaystyle O}{||}}{C}-PdL_n \longleftrightarrow R_2N-\overset{\overset{\displaystyle O^-}{|}}{C}\overset{+}{=}PdL_n$$
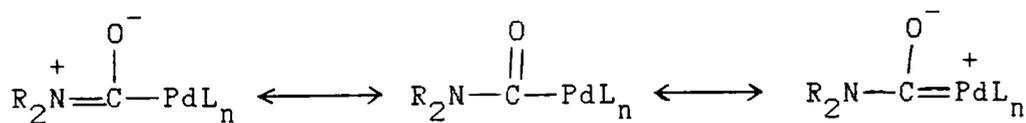
This effect is observed by a lowering of the carbonyl stretching frequency band to around 1600 cm^{-1}.

The remaining peaks cannot be assigned to any organic species found to be formed using this catalyst, nor can they be assigned to any palladium carbonyl species documented. These carbonyl stretching frequency bands may conceivably be due to species that are not involved in the main reaction pathway; they may instead represent a side reaction product. The peak at 1670 cm^{-1} is similar to the carbonyl stretching frequency bands for ureas, amides and formamides; these were however not observed in the product mixtures. The second peak at 1755 cm^{-1} is not characteristic of any particular nitrogen containing species and is presumably due to a carbonyl group bound to palladium.

The peak at around 2110 cm^{-1} may be due to either dissolved carbon monoxide or to a palladium carbonyl species. The design of the infra-red spectrometer accommodates a reference cell which should compensate for absorption by the solvent and dissolved gas. However the path lengths in the two cells were not easily matched and may, in fact, have been slightly imbalanced, particularly under pressure.

This would explain the peak in the 2100 cm^{-1} region due to dissolved carbon monoxide though it is normally centred at c.a. 2140 cm^{-1}. Another possible source of the band around 2100 cm^{-1} is a palladium carbonyl species. Cationic palladium (II)

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carbonyls such as $L_2Pd(CO)Cl^+$ give rise to carbonyl stretching frequency bands in this region and these compounds can be readily formed from a palladium (II) salt in a carbon monoxide atmosphere. The existence of these species cannot be positively identified using the current infra-red cell due to the reason stated above. However one may reasonably expect the formation of cationic species to occur.

Possible assignments for the two peaks at 1670 and 1755 cm^{-1} may arise from the formation of a double insertion species

i.e.

$$\begin{array}{cc} O & O \\ \parallel & \parallel \\ C - C \\ \diagup \quad \diagdown \\ R_2N \qquad NR_2 \end{array}$$

The carbonyl group adjacent to the nitrogen is expected to have a carbonyl stretching frequency at around 1660 cm^{-1} and the carbonyl group adjacent to the palladium to give a peak at around 1700-1800 cm^{-1}. Although double insertion products are known (9), their formation generally occurs under more forcing conditions and the formation of such species is therefore unlikely in the present system which involves mild conditions.

7.7. Discussion of the reaction mechanism

It seems reasonable on the basis of the more comprehensively studied carbonylation reaction of organo halides to postulate an analogous reaction pathway. These reactions involve oxidative addition of an organic halide, usually an aryl derivative, to zero valent palladium species:-

i.e. $Pd(PPh_3)_4$ + RX $\longrightarrow$ $Pd(PPh_3)_2(R)(X)$ + $2PPh_3$
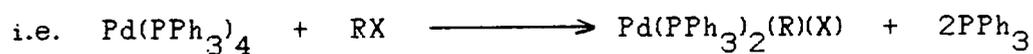
Under a carbon monoxide atmosphere this o-bonded aryl palladium

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species can undergo insertion of carbon monoxide to the acyl complex:-

$$Pd(PPh_3)_2(R)(X) + CO \longrightarrow Pd(PPh_3)_2(COR)(X)$$
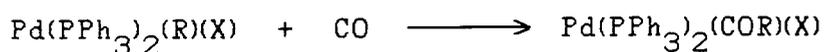
The reaction is believed to proceed via the formation, of a five co-ordinate palladium species, evidence coming from the lack of phosphine exchange in the reaction. The acyl complex thus generated may undergo either reductive elimination to give an acyl halide, or if an alcohol is present, alcoholysis to an ester with the formation of a hydrido-palladium species:-

i.e. $$Pd(PPh_3)_2(COR)(X) \longrightarrow RCOX + [Pd(PPh_3)_2]$$

$$Pd(PPh_3)_2(COR)(X) + R'OH \longrightarrow RCOOR' + Pd(PPh_3)_2HX$$
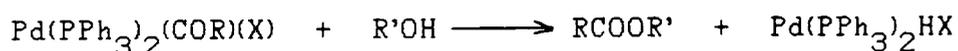
In the case of ester synthesis a base would have to be present to convert the hydrido-palladium species to a zero valent complex:-

$$Pd(PPh_3)_2HX + R_3N \xrightarrow{CO} Pd(PPh_3)_2(CO)_2 + R_3NHX$$
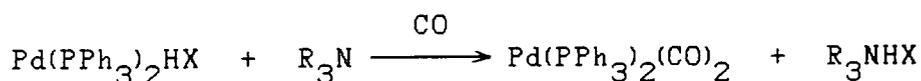
By postulating a similar reaction scheme for the carbonylation of N-chloroamines the reaction can be envisaged as being composed of three main steps:-

Step 1 oxidative addition

Step 2 carbon monoxide insertion

Step 3 reductive elimination

$$L_m Pd \Big\langle \begin{matrix} CONR_2 \\ Cl \end{matrix} \longrightarrow L_m Pd \ + \ R_2 NCOCl$$
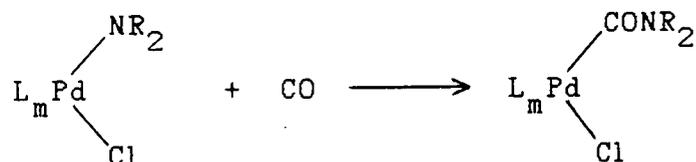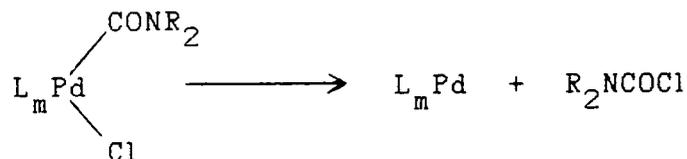
Each of these stages will be discussed in detail.

Step 1 oxidative addition

The oxidative addition step is certainly more complex than the single step suggested above. The reaction is far more likely to proceed through initial co-ordination of an N-chloroamine to a co-ordinatively unsaturated palladium complex. The resulting co-ordination complex may then undergo oxidative addition of the nitrogen-chlorine bond.

$$L_n Pd \ \rightleftharpoons \ L_{n-1} Pd \ + \ L$$

$$L_{n-1} Pd \ \rightleftharpoons \ L_{n-1} Pd \leftarrow :NR_2 \atop | \atop Cl$$

$$L_{n-1} Pd \leftarrow \begin{matrix} :NR_2 \\ | \\ Cl \end{matrix} \ \rightleftharpoons \ L_{n-2} Pd \Big\langle \begin{matrix} NR_2 \\ Cl \end{matrix} \ + \ L$$

(I)
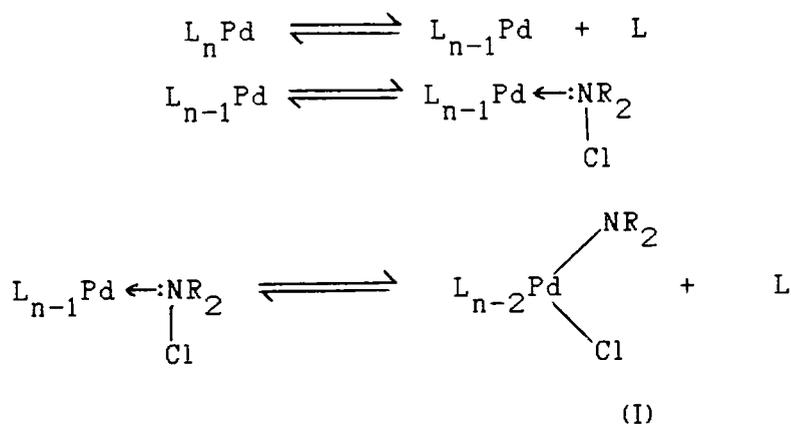
(L = CO, PPh$_3$ or solvent)

The disadvantage of proposing intermediates of the type (I) with $R_2 N^-$ ligands co-ordinated to palladium, is that these complexes have not been isolated to date: Indirect evidence for the existance of such complexes comes from the observation that N-chloroamine will react with palladium (O) compounds, namely tris(triphenylphosphine) palladium carbonyl, to give palladium dichloride complexes. This is envisaged to proceed via successive

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oxidative-addition of two N-chloroamines, followed by reductive

elimination of an organic molecule.

$$R_2NCl \quad PdL_n \longrightarrow L_nPd(Cl)NR_2 \xrightarrow{\;R_2NCl\;} L_nPdCl_2 + organic\ product$$
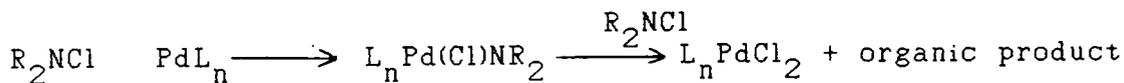
The alternative explanation for this observation is

formation of free chlorine by decomposition of the N-chloroamine.

The chlorine will then react with any palladium (0) complexes to

give palladium (II) dichloride complexes. Although N-chloroamines

are known to give free chlorine the reaction is only really

important when a strong acid is present, usually hydrogen

chloride. It is felt that under the conditions employed in this

work that chlorine elimination is of minor importance, and thus

the following reaction sequence is of little significance:-

$$2R_2N-Cl \longrightarrow R_2N-NR_2 + Cl_2$$
$$Cl_2 + L_nPd \longrightarrow L_2PdCl_2$$
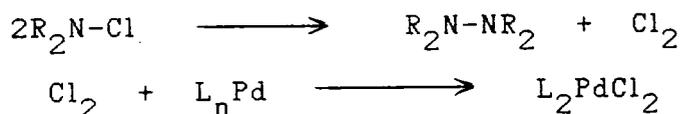
In this work, results have been obtained that are

consistent with the formation of co-ordinatively unsaturated

palladium species. The first observation is the levelling off in

the rate of carbon monoxide gas uptake as the pressure is

increased for the catalytic reaction (see Figure 6.2.). As one

increases the pressure there will be more carbon monoxide

molecules available for complex formation, thus competition

between carbon monoxide and N-chloroamines for co-ordination

sites will occur. As carbon monoxide is a better ligand than N-

chloroamine, due to the electron withdrawing effect of the

chlorine atom making the nitrogen atom a poorer o-donor, then

carbon monoxide will preferentially co-ordinate and thus reduce

the number of palladium nitrogen species for further reaction. The fact that as pressure increases the rate of gas uptake also increases, is explained by formation of the carboxamide complex in step 2 which is dependent on the concentration of carbon monoxide (and is thus favoured by an increase in pressure).

The second observation, which supports the involvement of co-ordinatively unsaturated palladium species, is the poisoning effect that relatively small amounts of amine bases have on the reaction. As mentioned above the N-chloroamine is a poor σ-donor due to the electron withdrawing effect of the chlorine atom. In comparison the amine base is a better ligand both on electronic grounds as stated and also on steric grounds, as the chlorine atom is bulky making the N-chloroamine molecule a sterically demanding ligand. Hence any amine present in solution will preferentially co-ordinate and thus reduce the number of palladium-N-chloroamine species, presumably to such an extent that the catalytic reaction virtually ceases.

$$R_2N-Cl \ + \ L_3Pd\leftarrow:NHR_2 \ \rightleftharpoons \ L_3Pd\leftarrow:\underset{\underset{Cl}{|}}{N}R_2 \ + \ RNH_2$$
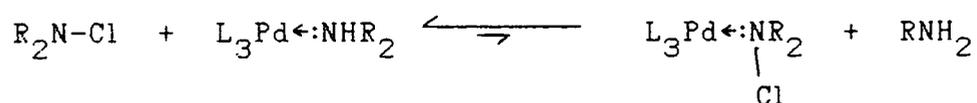
If the co-ordination of the N-chloroamine molecule or the oxidative addition of the chlorine nitrogen compound is a rate determining step, then any change in the number of such species will be reflected in the yields after a given reaction time. Thus if compounds are present with similar co-ordinating ability as N-chloroamines, then they may be expected to affect the yield of carbonylated products. This is in fact the situation found when one changes the reaction solvent to hetero-atom solvents such as

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monoglyme or acetonitrile, Saegusa (5) found that compared with benzene the above gave lower yields for similar reaction times.

Step 2 carbon monoxide insertion

The second step in he reaction involves the conversion of the amide complex $L_2Pd(Cl)NR_2$ into the carboxamide complex $L_2Pd(Cl)CONR_2$. Although this is classified as insertion of carbon monoxide, the process involves migration of the co-ordinated group onto the carbonyl group. In the present case this can be envisaged as internal nucleophilic attack of the R_2N^- ligand on the carbonyl group. This step of the reaction involves two processes, the first is ligand migration and the second co-ordination to the vacant site created:-

$$LPd(CO)(Cl)NR_2 \longrightarrow LPd(Cl)CONR_2$$

$$LPd(Cl)CONR_2 + L \longrightarrow L_2Pd(Cl)CONR_2$$

(L = CO, PPh_3 or solvent)
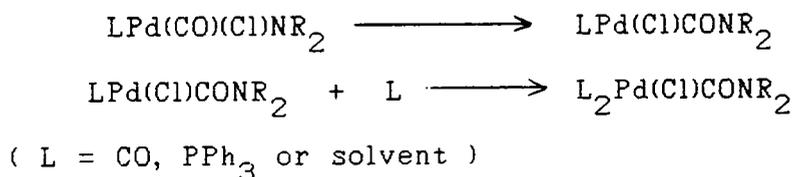
The reaction may be the two steps shown or could be a single step in which the incoming ligand may assist in the migration of the NR_2^- group.

Evidence for this step in the reaction comes from the isolation of palladium carboxamide complexes by Angelici (8). These complexes were initially prepared by two main routes, the first involved the reaction of a palladium (0) complex, i.e. tetrakis(triphenylphosphine) palladium, with a carbamoyl chloride. The second method requires reaction of bis(triphenylphosphine) palladium dichloride with an amine under a carbon monoxide atmosphere. Although for palladium no complexes exist without phosphine ligands for nickel such species are

known i.e. $[Me_2NCONi(CO)_3]^- Li^+$ (10).

The formation of hydrogen chloride in the reaction medium, via the decomposition of primary carbamoyl chloride, was found to depress the yield of carbonylated species.

$$RNHCOCl \longrightarrow RN=C=O + HCl$$
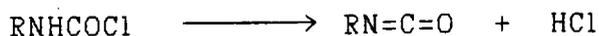
In the catalytic system hydrogen chloride causes protonation of the nitrogen in the carboxamide group, followed by loss of amine, which in the presence of acid is converted into the hydrogen chloride salt.

$$L_2Pd \overset{\displaystyle CONRH}{\underset{\displaystyle Cl}{<}} \xrightarrow{HCl} [L_2Pd(CO)Cl]Cl + RNH_2$$

$$RNH_2 + HCl \longrightarrow RNH_3Cl$$
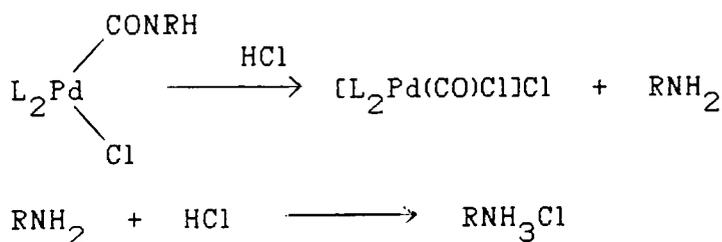
This production of hydrochloride salts accounts for the major by-product in the carbonylation of primary amines. It can best be explained by the above reaction; however there are two other possible explanations. The first is that there are significant quantities of free amine present in the initial N-chloroamine solution resultion from an inefficient chlorination stage. This is thought to be unlikely as the separate addition of an amine base was found to virtually suppress the catalytic reaction. Thus large quantities of amine cannot be initially present in the N-chloroamine.

The second possibility is that free amine is being formed continually in small quantities; this could arise via the following equilibrium:-

$$2RNHCl \rightleftharpoons RNH_2 + RNCl_2$$

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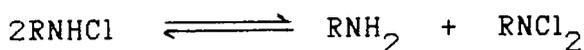
Although this reaction is reported to occur (17), it is thought
to be of minor importance under the conditions used in this
study. In a separate experiment a mixture of $\underline{t}$-octylamine and
N,N-dichloro-$\underline{t}$-octylamine were stirred together at room
temperature in diethylether for several days, but no trace of N-
chloro-$\underline{t}$-octylamine could be detected by infra-red spectroscopy.

The carboxamide complex can exist in two isomeric forms;
these are $\underline{cis}$ and $\underline{trans}$ square planar complexes:-

$$
\begin{array}{cc}
L\diagdown \diagup Cl & Cl\diagdown \diagup L \\
Pd & Pd \\
L\diagup \diagdown CONR_2 & L\diagup \diagdown CONR_2 \\
\underline{cis}\ (IIa) & \underline{trans}\ (IIb)
\end{array}
$$
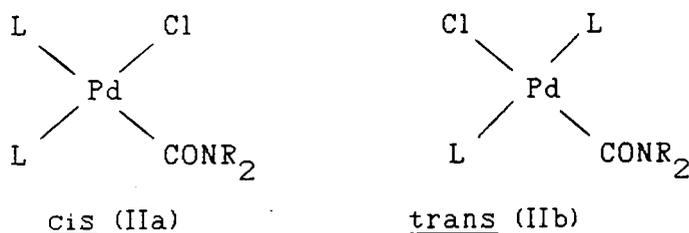
The formation of both of these complexes is possible in the
catalytic system, however these isomers do not have equal
stabilities. If the ligands are bulky then the most favourable
isomer is the $\underline{trans}$ form (IIb) this was the isomer isolated by
Angelici (8) with no mention being made of the $\underline{cis}$ complex
(IIa).

The poor yield of the $\underline{trans}$-carboxamide complex formed by
reaction of tetrakis(triphenylphosphine) palladium with dimethyl
carbamoyl chloride, may be related to the lower stability of the
corresponding $\underline{cis}$ complex. The $\underline{cis}$ complex will be initially
formed by oxidative addition of the carbamoyl chloride, which may
then isomerise to give the observed product, the $\underline{trans}$ complex.
However as the major product was the $(PPh_3)PdCl_2$ complex the $\underline{cis}$
carboxamide complex must undergo further reaction in preference

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to isomerisation. The interconversion of the <u>cis</u> and <u>trans</u>

complexes must therefore be relatively slow. Isomerisation can

occur by two mechanisms either by ligand displacement, via

formation of a pentavalent intermediate:-

$$
\begin{array}{c}
L \diagdown \quad \diagup Cl \\
Pd \\
L \diagup \quad \diagdown CONR_2
\end{array}
\quad \xrightarrow{L'} \quad
\left[
\begin{array}{c}
L \\
L' \diagdown \;| \\
\quad \diagup Pd-Cl \\
L \diagup \;| \\
\quad CONR_2
\end{array}
\right]
\quad \xrightarrow{-L} \quad
\begin{array}{c}
L' \diagdown \quad \diagup Cl \\
Pd \\
R_2NCO \diagup \quad \diagdown L
\end{array}
$$
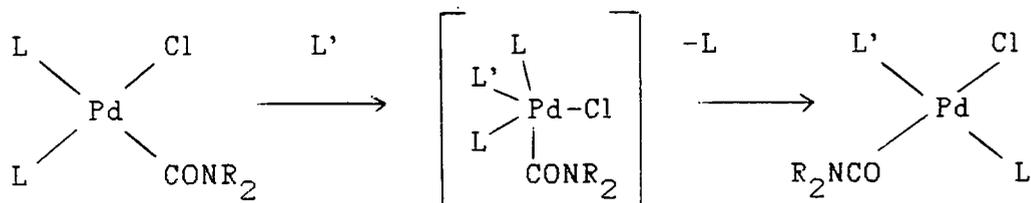
or through the formation of a trivalent complex by ligand

elimination

$$
\begin{array}{c}
L \diagdown \quad \diagup Cl \\
Pd \\
L \diagup \quad \diagdown CONR_2
\end{array}
\quad \xrightarrow{-L} \quad
\begin{array}{c}
\quad \diagup Cl \\
L-Pd \\
\quad \diagdown CONR_2
\end{array}
\quad \xrightarrow{L} \quad
\begin{array}{c}
L \diagdown \quad \diagup Cl \\
Pd \\
R_2NCO \diagup \quad \diagdown L
\end{array}
$$
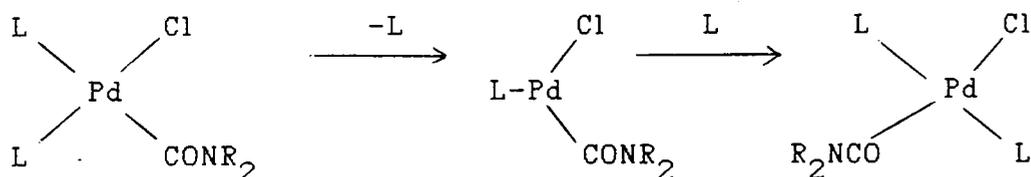
(L = CO, PPh_3 or solvent)

Step 3 reductive elimination

The final step in the reaction mechanism is reductive

elimination of the carbamoyl chloride to give a co-ordinatively

unsaturated palladium species:-

$$
L_2Pd(Cl)CONR_2 \quad \longrightarrow \quad L_2Pd + R_2NCOCl
$$
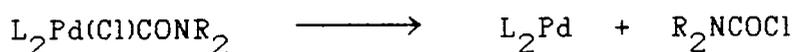
This reductive elimination is easier for the <u>cis</u> complex than the

<u>trans</u> form which has a less favourable arrangement of ligands.

For product formation to occur from the <u>trans</u> complex isomer-

isation to the <u>cis</u> form must first occur, this as mentioned above

will be a slow reaction.

In the case of mono-alkyl-N-chloroamines there are two

possible organic products, namely carbamoyl chloride and iso-

cyanate; the latter formed by loss of hydrogen chloride from the

carbamoyl chloride. Both of these products are observed from the

reaction of phosgene and a primary amine, however formation of large quantities of isocyanate requires the presence of a base and heating.

$$RNH_2 \ + \ COCl_2 \ \longrightarrow \ RNHCOCl \ + \ HCl \ \xrightarrow[\text{Heat}]{\text{Base}} \ RNCO \ + \ HCl$$
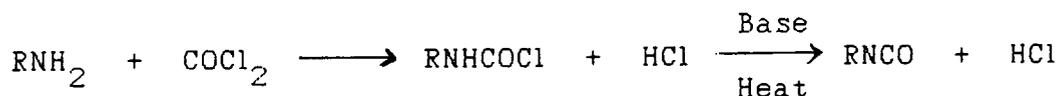
For the catalytic system a different route to isocyanates exists, which involves a [1,3]-hydride shift occurring for either cis or trans carboxamide complexes:-
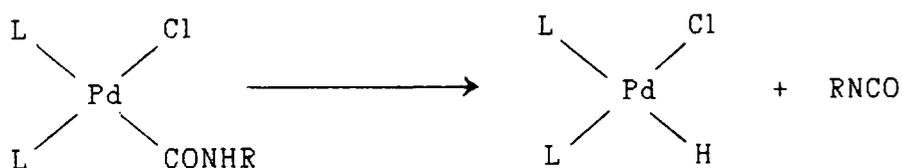
[1,3]-hydride shifts are well known for other catalytic reactions, and in the case of metal alkyl complexes this process leads to the formation of alkenes. This reaction is not normally found for metal acyl complexes, however, as the products formed would be ketenes a process which is not thermodynamically very favourable. In the present case, involving palladium carboxamide complexes, the hydrogen is more labile due to the weaker nitrogen-hydrogen bond compared with the carbon-hydrogen bond. The observation that carbamoyl chloride formation still occurs suggests that this process of [1,3]-hydride shift does not occur exclusively and that reductive elimination must still be considered. Attempts to validate the mechanism, by reaction of phenyl carbamoyl chloride with tris(triphenylphosphine) palladium carbonyl, failed as the only process observed was oxidation of palladium to palladium (II) dichloride complexes with no isocyanate peak being observed in the infra-red. This mechanism

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may still be applicable and it is conceivable that given the right conditions, possibly a carbon monoxide atmosphere and by a suitable choice of a palladium complex, that this [1,3]-hydride shift may occur to give high yields of isocyanates.

Initiation of the catalytic cycle

One of the main mechanistic points not considered so far is the formation of suitable palladium species to initiate the catalytic reaction cycle. In the case of palladium metal, as catalyst precursor, straight oxidative-addition of an N-chloroamine can be envisaged. N-chloroamines are strong oxidising agents, as was observed by the oxidation of $(PPh_3)_3Pd(CO)$ to palladium (II) chloride complexes. Also palladium metal is known to react with acid chlorides in the presence of triphenylphosphine to give an acyl complex (11):-

$$RCOCl + Pd \xrightarrow{PPh_3} (PPh_3)_2Pd(COR)Cl$$
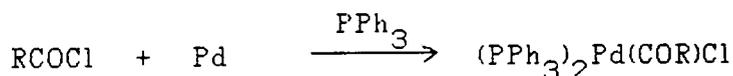
In the present system, oxidative-addition of an N-chloroamine is proposed; which together with carbon monoxide could generate the carboxamide complex:-

$$Pd + R_2NCl \xrightarrow{L} L_2Pd \overset{Cl}{\underset{NR_2}{<}} \xrightarrow{CO} L_2Pd \overset{Cl}{\underset{CONR_2}{<}}$$
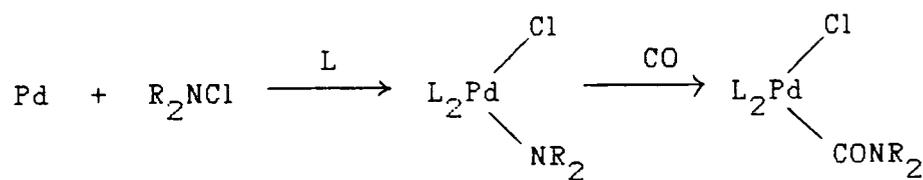
(L = CO, PPh_3 or solvent)

However in the case of palladium (II) salts the mechanism for reduction to palladium (0) or the formation of a carboxamide complex is not easily envisaged. Reduction of a palladium (II) species requires the use of a reducing agent, in the present system the only reducing agent is carbon monoxide. This however

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is not generally thought to be capable of accomplishing this reaction itself but also requires the presence of another reducing agent. Common reducing agents used to prepare palladium (0) species are sodium borohydride, hydrazine, copper metal and organometallic species such as the alkyl aluminiums (12):-

$$L_2PdX_2 \; + \; BH_4^- \; \longrightarrow \; [PdL_2]$$

$$2L_2PdCl_2 \; + \; 4L \; + \; 5N_2H_4 \; \longrightarrow \; 2PdL_4 \; + \; 4N_2H5Cl \; + \; N_2$$

$$PdCl_2 \; + \; 4L \; + \; Cu \; \longrightarrow PdL_4$$

$$Pd(acac)_2 \; + \; Et_3Al \; + \; 4L \; \longrightarrow \; PdL_4$$

(L = phosphine or phosphite)
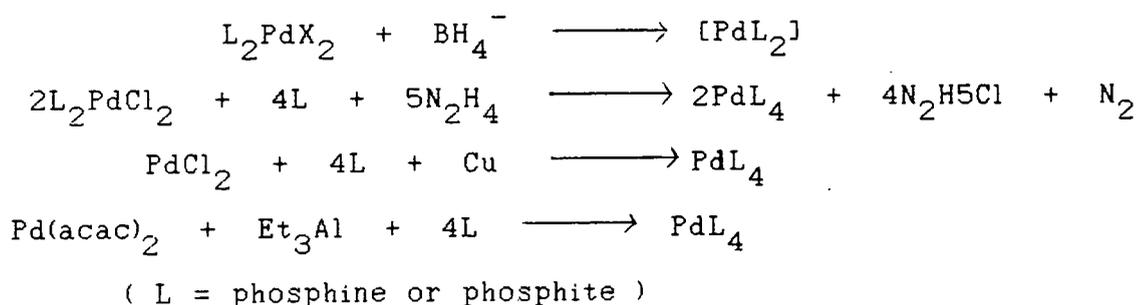
Under a carbon monoxide atmosphere the above methods can be modified, to give substituted carbonyl phosphine complexes of palladium, usually the tris(triphenylphosphine) palladium carbonyl complex.

In the reaction under study there are no suitable reducing agents and hence another mechanism must be occurring. One possible route involves palladium intermediates of the type $[L_2Pd(CO)Cl]^+$. Related species $[L_2Pt(CO)Cl]^+$ can react with nucleophilic ligands such as alcohols and amines. Evidence for this type of reaction comes from the ready formation of $[L_2Pt(CO)Cl]^+$ from $[L_2PtCl_2]$, by the action of carbon monoxide at room temperature. This type of mechanism involves nucleophilic attack at the co-ordinated carbon monoxide ligand. The reaction is facilitated by the positive charge making the carbon of the co-ordinated carbon monoxide ligand more susceptible to nucleophilic attack via electron withdrawal.
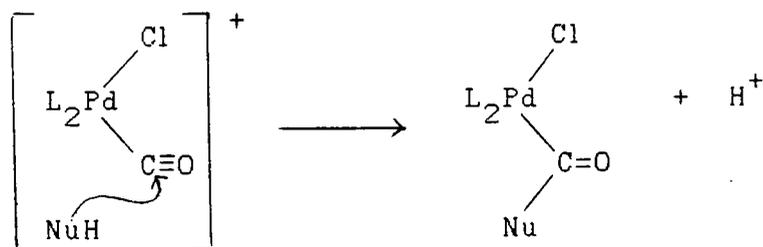
One disadvantage to applying this type of mechanism to N-chloroamines is again their poor nucleophilicity; the chlorine atom reduces the electron density around the nitrogen atom and hence makes it less nucleophilic. Another disadvantage is that transfer of a chlorine or alkyl group would have to occur. If an alkyl group were transfered to the metal then the product would not be a dialkyl carbamoyl chloride but would be an N-chloro-carbamoyl chloride. For chlorine migration the complex which resulted would formally be a palladium (IV) complex.
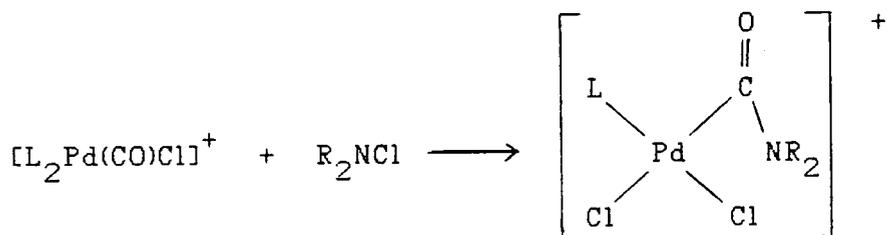
This complex could then lose chlorine to give the carboxamide complex. However this is thought to be unlikely. Palladium (IV) complexes are relatively few in number and are usually only stable in the presence of hard Lewis bases such as amines. If elimination of carbamoyl chloride occurred from this complex, then the palladium species formed could pick up carbon monoxide and regenerate the $[L_2Pd(CO)Cl]^+$ species. This gives an alternative mechanism based on a palladium (II) palladium(IV) cycle.

The strong oxidising power of N-chloroamines suggests an

alternative mechanism to form carboxamide complexes. This
mechanism also involves the formation of a palladium (IV) complex
via oxidative addition of N-chloroamine to generate a $Pd(NR_2)Cl_3$
species. This could then undergo reductive elimination of
chlorine to form a carboxamide complex, after insertion of carbon
monoxide into the palladium nitrogen bond:-

i.e. $PdCl_2$ + R_2N-Cl $\rightleftharpoons$ $PdCl_3(NR_2)$ $\rightleftharpoons$ $PdCl(NR_2)$

$PdCl(NR_2)$ + CO $\longrightarrow$ $Pd(CONR_2)Cl$
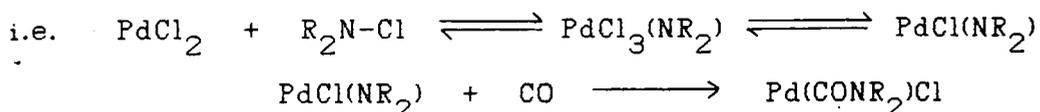
Support for this type of process comes from the ready
formation of palladium (IV) complexes from palladium (II)
complexes by the action of elemental chlorine. These species are
only stable in solution in the presence of an excess of chlorine.
The presence of the R_2N^- ligand will also help stabilise these
complexes. As mentioned before palladium (IV) complexes are
stabilised by hard Lewis bases. The stabilisation of high
oxidation states by hard Lewis bases is a common feature in
transition metal chemistry. The highest oxidation states for
manganese, for instance occur with oxygen ligands i.e. MnO_4^-. The
stabilisation caused by these ligands arises from their ability
to donate electron density to the metal centre through p-orbital
interaction with the metal d-orbitals.

i.e.
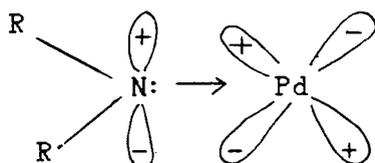
The R_2N^- ligand also donates electron density via o-bond
formation, thus this ligand can act as a 4 electron donor.
Stabilisation of palladium (IV) species by chlorine is also

presumably due to $p\pi - d\pi$ interaction of the metal with the chlorine p-orbitals.

Platinum, on the other hand, has a large number of known platinum (IV) complexes. There are several routes to platinum (IV) complexes which include halogen oxidation of platinum (II) complexes, oxidative addition of metal halides, alkylation of platinum (IV) and oxidation with acyl or alkyl halides of platinum (II) (13).

i.e. $[Pt(PEt_3)_2MeI] + MeI \longrightarrow Pt(PEt_3)_2Me_2I_2$
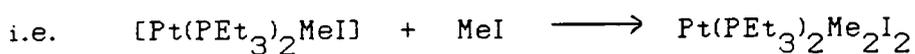
This reaction is not observed with palladium however, presumably due to the relative instability of palladium (IV) species. In the case of N-chloroamines the N-Cl bond is relatively weak and these compounds are strong oxidising agents, thus one would expect a similar reaction, to that above, to occur at least for platinum and possibly for palladium also. Even if the reaction is an equilibrium then due to the removal of the $L_2Pd(NR_2)(Cl)$ species, by further reaction, then the equilibrium will be forced to the right:-

$"PdCl_2" + R_2NCl \rightleftharpoons "PdCl_3NR_2" \rightleftharpoons "PdCl(NR_2)" + Cl_2$
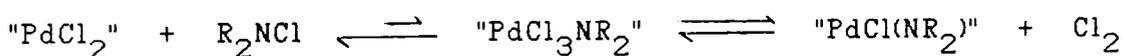
This initiation mechanism is thought to be more likely than the alternative reaction mechanism based on the following palladium (II)/palladium (IV) cycle:-

$[L_2Pd(CO)Cl]^+ + R_2N-Cl \longrightarrow [LPd(CONR_2)Cl_2]^+ + L$

$[LPd(CONR_2)Cl_2]^+ \longrightarrow [LPdCl]^+ + R_2NCOCl$
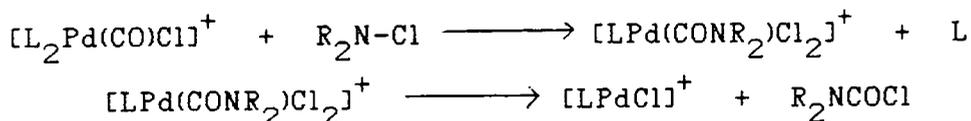
Overall reaction scheme

The indirect evidence for the involvement of carboxamide complexes leads to the following reaction scheme for the

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catalytic reaction:-

$$[L_2PdCl_2]$$

$$L \uparrow \quad \downarrow -L$$

$$[LPdCl_2]$$

$$-R_2NCl \uparrow \quad \downarrow R_2NCl$$

$$[PdCl_3(NR_2)]$$

$$-2L,+Cl_2 \uparrow \quad \downarrow -Cl_2,+2L$$

$$[L_2PdClNR_2]$$

Proposed reaction scheme for the catalytic carbonylation

of N-chloroamines

By-product formation

The only by-product observed was the amine hydrochloride,
which was only obtained when primary amines were used. Generally
when amines are carbonylated a number of products are observed,
these include ureas, formamides and hydrazines. In the present
system none of these compounds were detected; this is not
surprising for the formation of formamides requires a hydrogen

source to be present. For the other two compounds one can

envisage mechanisms leading to such species and in the case of

hydrazines both with and without palladium mediation.

Hydrazine synthesis not involving palladium can be

envisaged as occurring by direct reaction of two N-chloroamines.

$$2R_2NCl \longrightarrow R_2N-NR_2 + Cl_2$$
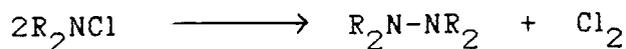
A similar reaction applies to N-chloroamines and an amine (14)

$$R_2NCl + R'_2NH \longrightarrow R_2N-NR'_2.HCl$$

This reaction presumably occurs via nucleophilic attack of the

amine on the nitrogen of the N-chloroamine. This would explain

why this reaction is not observed for N-chloroamines themselves,

as the chlorine atom greatly reduces the nucleophilic tendency of

these compounds.

The palladium mediated synthesis route would also have to

involve nucleophilic attack of an N-chloroamine, this time on the

imido palladium complex.

$$R_2NCl + L_nPd \underset{Cl}{\overset{NR_2}{<}} \longrightarrow L_nPdCl_2 + R_2N-NR_2$$
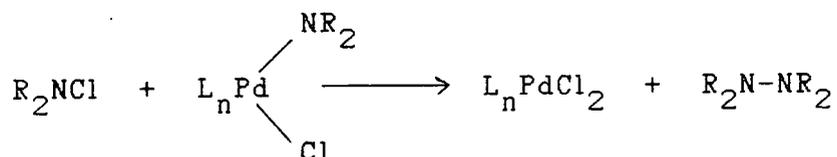
The poor nucleophilicity of N-chloroamines makes this reaction

unlikely to occur in the present case and was also not observed

by Ryang with nickel tetracarbonyl (7).

In Ryang's work, with nickel tetracarbonyl and dimethyl N-

chloroamine, the major product was the corresponding urea. This

can be envisaged as occurring by the following mechanism:-

Cl   Cl
                 /   /
    (CO)$_2$Ni $\longrightarrow$ (CO)$_2$Ni   O$^-$
                 \   \   \
                  CO   \$^+$/ C
              / \   R$_2$NCl   NR$_2$
        R$_2$N-Cl NR$_2$

                                                          | [1,3] Hydride shift
                                                          ↓

                        L$_2$NiCl$_2$ +   R$_2$NCONR$_2$
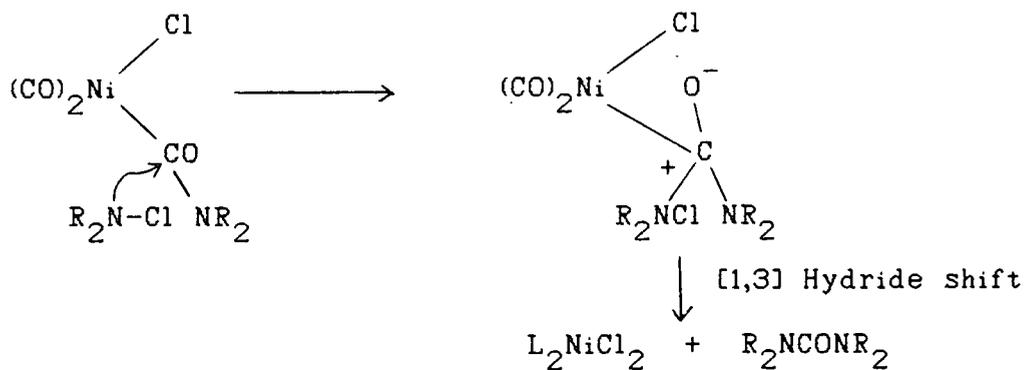
In the present system this reaction is of minor importance;
the difference between nickel and palladium is not at first sight
obvious. The presence of the carbon monoxide atmosphere for the
catalytic palladium system may play a part, although the main
reason is probably differences in the susceptibility to nucleo-
philic attack of the carboxamide complexes. These complexes can
be envisaged as being a combination of three canonical forms:-

           O$^-$ O   O$^-$
     $^+$ | || | $^+$
    L$_2$M = C - NR$_2$ $\longleftrightarrow$ L$_2$M - C - NR$_2$ $\longleftrightarrow$ L$_2$M - C = NR$_2$

    (M = Ni or Pd)
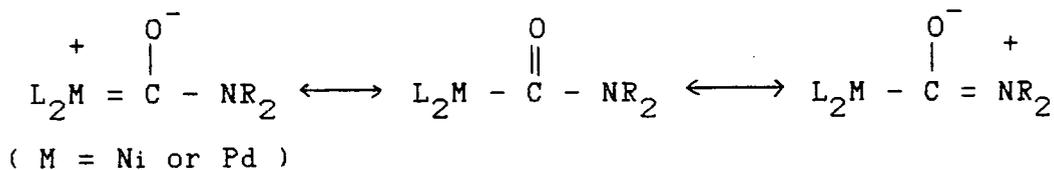
The importance of each form will be dependant on the amine
and on the metal in question. E.g. if the metal in question is
electron deficient then the first canonical form will be the
least favourable, hence the resulting chemistry of this complex
can be best described in terms of the latter two forms. A similar
effect can also occur for the carbamoyl chlorides themselves and
explains their relative stability compared to acid chlorides
towards nucleophilic attack.

Alternative mechanisms

The main alternative mechanism that can be proposed
involves species such as $[L_nPd(CO)Cl]^+$ and is discussed in the

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section under initiation mechanisms. This is thought to be unlikely as it involves palladium (IV) intermediates without suitable stabilising ligands, such as R_2N^-. One other possibility is formation of phosgene in solution from the carbon monoxide atmosphere and N-chloroamines or from L_2PdCl_2. The latter route was not supported by Stern's work (15). The generation of phosgene from N-chloroamines is also not observed and concomitant formation of amines is excluded by the lack of poisoning of the palladium catalyst which normally occurs with amines.

Application of carboxamide complexes to other processes

The involvement of carboxamide complexes can also be used to explain the reaction mechanisms involved in Stern's work (15) and in a patent by I.C.I. for production of urethanes (16).

In the case of Stern's work (15) the palladium (II) chloride used in the presence of carbon monoxide and the amine, would be converted according to Angelici et al to the carboxamide complex. This would then undergo reductive elimination to the carbamoyl chloride.

$$PdCl_2 \;+\; CO \;+\; RNH_2 \;\longrightarrow\; L_2Pd\underset{C=O}{\overset{Cl}{\diagup\!\!\diagdown}} \;+\; HCl$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\ NRH$$

$$L_2Pd\underset{C=O}{\overset{Cl}{\diagup\!\!\diagdown}} \;\cdot\; \longrightarrow\; [L_2Pd] \;+\; RNHCOCl$$
$$\quad |$$
$$\ NRH$$

$$RNHCOCl \;\longrightarrow\; RNCO \;+\; HCl$$
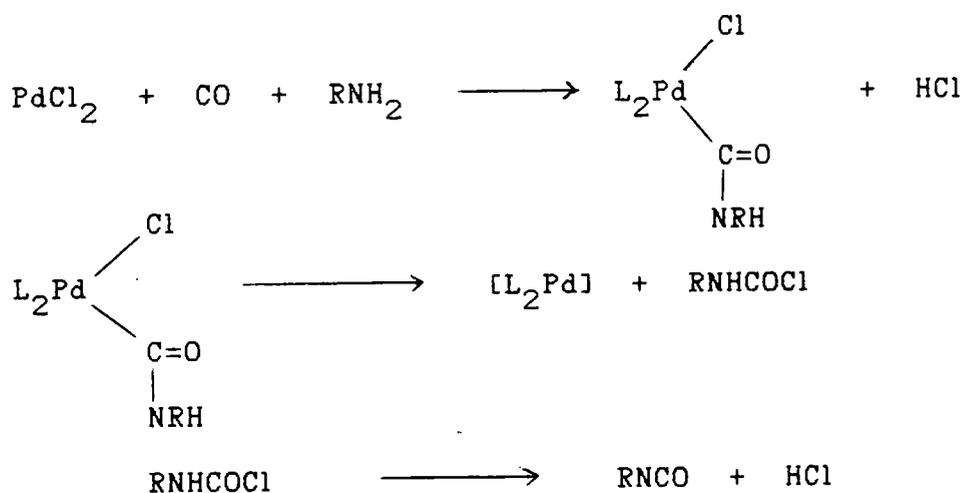
In this reaction the base employed was disodium hydrogen

phosphate, which would remove any hydrogen chloride formed and thus prevent decomposition of the intermediate carboxamide complex. This reaction is however stoichiometric, the palladium (II) salt being reduced to palladium (0).

A similar mechanism is applicable to the I.C.I. patented process (16). In this system the palladium complex is initially in the zero valent state, however the gas mixture used was carbon monoxide and oxygen which would efficiently oxidise the palladium (0) to palladium (II). The remainder of the mechanism is essentially the same except that, as an alcohol was used as a solvent, the isocyanate was not isolated but converted 'in-situ' into the corresponding urethane.

$$Pd^{2+} \quad + \quad RNH_2 \quad \xrightarrow[\text{EtOH,CsI}]{\text{CO/O}_2} \quad Pd \quad + \quad RNHCOOEt$$
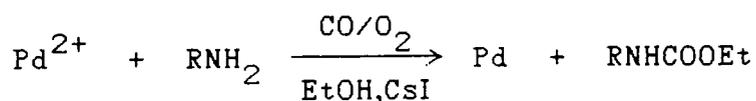
7.8. Summary

Although no direct evidence for the existance of the carboxamide complex was found, by 'in-situ' infra-red spectroscopy, supporting evidence for its involvement come from the formation of such complexes by the reaction of a zero valent palladium species and a carbamoyl chloride. The formation of significant quantities of amine hydrochloride, in the case of primary amines, can only be accounted for if one postulates the presence of carboxamide complexes in solution.

The reaction of a zero valent palladium species with an N-chloroamine to form an $L_2PdClNR_2$ complex, is supported by this work, but under the conditions employed, a further reaction takes place to yield palladium (II) dichloride:-

$$[L_4Pd] \xrightarrow{R_2NCl} \left[L_2Pd \begin{array}{c} Cl \\ \diagup \\ \diagdown \\ NR_2 \end{array} \right] \xrightarrow{R_2NCl} L_2PdCl_2$$
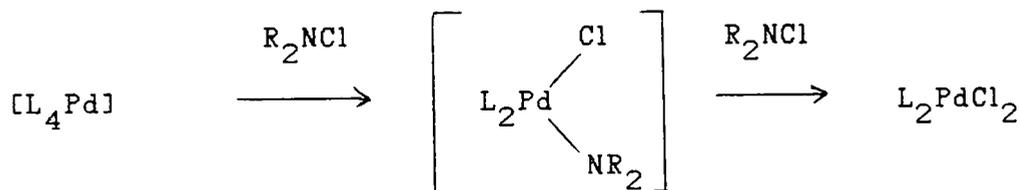
The formation of such species can only occur if oxidative addition of the nitrogen-chlorine compound has occurred. This reaction requires the presence of co-ordinatively unsaturated palladium species in solution. In the case of phosphine ligands equilibration is rapid as these ligands are quite labile. The participation of co-ordinatively unsaturated complexes is supported by the observation of the levelling of the rate of uptake of carbon monoxide as the pressure increases. If co-ordinatively unsaturated species are involved then the carbon monoxide will compete with N-chloroamine for co-ordination sites. As the latter is a poor ligand, due to the electron withdrawing

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effect of the chlorine and the bulk of this hetero-atom; Then preferential co-ordination by carbon monoxide is likely, thus blocking co-ordination sites for the N-chloroamine. The initial increase in the rate of carbon monoxide uptake as the pressure is increased may reflect the increasing stability of the palladium (O) complexes, or may be due to an increase in the rate of carbonylation,via carbon monoxide insertion, to form the carbox-amide complex. The latter explanation is thought to be more likely.

The involvement of co-ordinatively unsaturated species can also explain the apparent total suppression of reaction if any appreciable quantity of amine is present in the reaction system; also the yields are lower when hetero-atom solvents such as acetonitrile and monoglyme are used. The explanation for these observations is, as before, competition for co-ordination sites between the N-chloroamine and the above compounds. In the case of the hetero-atom solvents although their donating ability may be similar to, or less than, that of the N-chloroamine they are present in a large excess, and hence compete for co-ordination sites by sheer weight of numbers.

7.9. Conclusion

The work detailed in the previous chapter has shown the carbonylation of N-chloroamines to be a useful synthetic route to carbamoyl chlorides. The method employed does not suffer from the formation of a wide variety of carbonylated amine species normally found in catalytic reactions involving amines; namely one does not observe production of significant quantities of ureas.

The major by-product observed, primarily occurring when mono-alkyl-mono-chloro-amines are used, is amine hydrochloride and accounts for the lower yields obtained when using primary amines. This lowering in yield is not a result of the different nature of the amine, but is due to the formation of hydrogen chloride which causes decomposition of catalytic palladium species involved in the reaction. In this case, i.e. primary amines, the synthetic route is analogous to the classical organic route to carbamoyl chloride and isocyanates, in as much as a minimum of 50% of the feed amine is converted into hydrochloride salts.

The mechanism involved in this reaction, at first sight, looks very similar to the proposed scheme for the carbonylation of aryl halides; if such a mechanism is employed then some of the catalytic species indicated by such a scheme are unknown for palladium complexes. One of the proposed intermediates, namely $L_2PdCl(CONRR')$ is not observable by 'in-situ' infra-red spectroscopy; however this does not mean that such species are not present in small quantities. The experimental results

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obtained on the whole are in agreement with the scheme with this scheme and alternative mechanisms do not, in general, involve realistic catalytic intermediates. One of the main disadvantages to this scheme is the formation of a suitable catalytic species form a palladium (II) salt. A suggested solution to this problem involves the postulation of a palladium (II)/palladium (IV) cycle, which is entirely plausible given the strong oxidising ability of N-chloroamines and the observation that chlorine can oxidise palladium (II) to palladium (IV). The proposed R_2N^- ligand will also stabilise the higher oxidation state and hence aid this type of reaction.

The reaction between N-chloroamines and transition metal species has not been well studied and this investigation suggests that further study in this area is warranted. In the present study carbon monoxide was used as a small molecule to be inserted into the nitrogen-chlorine bond. However reactions of this type can often lead to the insertion of other species such as alkenes, alkynes etc. Thus the potential exists for the formation of other nitrogen containing species starting from N-chloroamines. For example, a reaction may occur between N-chloroamine and an alkene to give an unsaturated amine and hydrogen chloride.

i.e. $$CH_2=CH_2 \ + \ R_2N-Cl \ \xrightarrow{T_M} \ R_2N-CH=CH_2 \ + \ HCl$$
$$or$$
$$R_2NCH_2CH_2Cl$$
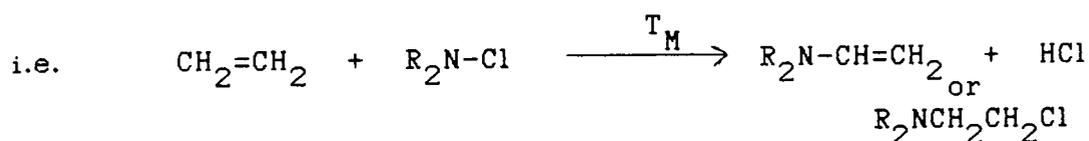
CHAPTER SEVEN - REFERENCES

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APPENDIX

RESEARCH COLLOQUIA, SEMINARS AND LECTURES

A. <u>Lectures and seminars organised by the Department of Chemistry during the period 1982-1985</u> (+ denotes lectures attended)

13.10.82[+]   Dr. W.J. Feast (Durham)
"Approaches to the synthesis of conjugated polymers"

14.10.82   Prof. H. Suhr (Tubingen,FRG)
"Preparative chemistry in nonequilibrium plasmas"

27.10.82[+]   Dr. C.E. Housecroft (Oxford High School/Notre Dame)
"Bonding capabilities of butterfly-shaped Fe_4 units.
Implications for C-H bond activation in hydrocarbon complexes"

28.10.82[+]   Prof. M.F. Lappert, FRS. (Sussex)
"Approaches to asymmetric synthesis and catalysis using electron-rich olefins and some of their metal complexes"

15.11.82[+]   Dr. G. Bertrand (Toulouse, France)
"Curtius rearrangement in organometallic series:
A route for new hybridised species"

24.11.82[+]   Prof. F.R. Hartley (R.M.C.S., Shrivenham)
"Supported metal-complex hydroformylation catalysts"

24.11.82[+]   Prof. G.G. Roberts (Applied Physics, Durham)
"Langmuir-Blodgett films: Solid state polymerisation of diacetylenes"

8.12.82[+]   Dr. G. Wooley (Trent)
"Bonds in transition metal-cluster compounds"

12. 1.83[+]   Dr. D.C. Sherrington (Strathclyde)
"Polymer-supported phase transfer catalysts"

9. 2.83[+]   Dr. P. Moore (Warwick)
"Mechanistic studies in solution by stopped flow F.T.-NMR and high pressure NMR line broadening"

21. 2.83   Dr. R. Lynden-Bell (Cambridge)
"Molecular motion in the cubic phase of NaCN"

2. 3.83[+]   Dr. D. Bloor (Queen Mary College, London)
"The solid- state chemistry of diacetylene monomers and polymers"

8. 3.83[+]   Prof. D.C. Bradley, FRS (Queen Mary College, London)
"Recent developments in organo-imido-transition metal chemistry"

9. 3.83   Dr. D.M.J. Lilley (Dundee)
"DNA, sequence, symmetry, structure and supercoiling"

11. 3.83[+]   Prof. H.G. Vieche (Louvain, Belgium)
"Oxidations on sulpur" and
"Fluorine substitutions in radicals"
(The W.K.R. Musgrave Lecture)

16. 3.83[+]   Dr. I. Gosney (Edinburgh)
"New extrusion reactions: Organic synthesis in a hot-tube"

25. 3.83   Prof. F.G. Baglin (Nevada, USA)
"Interaction induced Raman Spectroscopy in supracritical ethane"

21. 4.83   Prof. J. Passmore (New Brunswick, Canada)
"Novel selenium-iodine cations"

4. 5.83[+]   Prof. P.H. Plesch (Keele)
"Binary ionisation equilibria between two ions and two molecules. What Ostwald never thought of"

10. 5.83   Prof. W. Burger (Munich, FRG)
"New reaction pathways from trifluoromethyl-substituted heterodienes to partially fluorinated heterocyclic compounds"

11. 5.83[+]   Dr. N. Isaacs (Reading)
"The application of high pressures to the theory and practice of organic chemistry"

13. 5.83[+]   Dr. R. de Koch (Michigan/Amsterdam)
"Electronic structural calculations in organo-metallic cobalt cluster molecules. Implications for metal surfaces"

13. 5.83[+]   Dr. T.B. Marder (UCLA/Bristol)
"The chemistry of metal-carbon and metal-metal multiple bonds"

16. 5.83[+]   Prof. R.J. Lagow (Texas, USA)
"The chemistry of polylithium organic compounds. An unusual class of matter"

18. 5.83[+]   Dr. D.M. Adams (Leicester)
"Spectroscopy at very high pressures"

25. 5.83   Dr. J.M. Vernon (York)
"New heterocyclic chemistry involving lead tetraacetate"

15. 6.83   Dr. A. Pietrzykowski (Warsaw/Strathclyde)
"Synthesis, structure and properties of aluminoxanes"

22. 6.83   Dr. D.W.H. Rankin (Edinburgh)
"Floppy molecules - the influence of phase on structure

5. 7.83[+]   Prof. J. Miller (Camfinas, Brazil)
"Reactivity in nucleophilic substitution reactions"

5.10.83[+]   Prof. J.P. Maier (Basel, Switzerland)
"Recent approaches to spectroscopic characteriz-ation of cations"

12.10.83   Dr. C.W. McLeland (Port Elizabeth, Australia)
"Cyclization of aryl alcohols through the inter-mediacy of alkoxy radicals and aryl radical cations"

19.10.83   Dr. R.H. Alcock (Warwick)
"Aryl tellurium (1V) compounds, patterns of primary and secondary bonding"

26.10.83[+]   Dr. R.H. Friend (Cavendish, Cambridge)
"Electronic properties of conjugated polymers"

30.11.83[+]   Prof. I.M.G. Cowie (Stirling)
"Molecular interpretation of non-relaxation processes in polymerglasses"

2.12.83[+] Dr. G.M. Brooke (Durham)
"The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoro-aryl and -heteroaryl systems"

14.12.83[+] Prof. R.J. Donovan (Edinburgh)
"Chemical and physical processes involving the ion-pair states of the halogen molecules"

10. 1.84[+] Prof. R. Hester (York)
"Nanosecond laser spectroscopy of reaction intermediates"

18. 1.84[+] Prof. R.K. Harris (UEA)
"Multi-nuclear solid state magnetic resonance"

8. 2.84 Dr. B.T. Heaton (Kent)
"Multi-nuclear NMR studies"

15. 2.84 Dr. R.M. Paton (Edinburgh)
"Heterocyclic syntheses using nitrile sulphides"

7. 3.84 Dr. R.T. Walker (Birmingham)
"Syntheses and biological properties of some 5-substituted uracic derivatives; yet another example of serendipity in anti-viral chemotherapy"

21. 3.84[+] Dr. P. Sherwood (Newcastle)
"X-ray photoelectron spectroscopic studies of electrode and other surfaces"

21. 3.84[+] Dr. G. Beamson (Durham/Kratos)
"EXAFS: General principles and applications"

23. 3.84[+] Dr. A. Ceulemans (Leuven)
"The development of field- type models of the bonding in molecular clusters"

2. 4.84[+] Prof. K. O'Driscoll (Waterloo)
"Chain ending reactions in free radical polymerisation"

3. 4.84[+] Prof. C.H. Rochester (Dundee)
"Infrared studies of adsorption at the solid-liquid interface"

25. 4.84 Dr. R.M. Acheson (Biochemistry, Oxford)
"Some heterocyclic detective stories"

27. 4.84 Dr. T. Albright (Houston, U.S.A.)
"Sigmatropic rearrangements in organometallic chemistry"

14. 5.84 Prof. W.R Dolbier (Florida, U.S.A.)
"Cycloaddition reactions of fluorinated allenes"

16. 5.84 Dr. P.J. Garratt (UCL)
"Synthesis with dilithiated vicinal diesters and carboximides"

22. 5.84[+] Prof. F.C. de Schryver (Leuven)
"The use of luminescence in the study of micellar aggregates" and
"Configurational and conformational control in excited state complex formation"

23. 5.84 Prof. M. Tada (Waseda, Japan)
"Photochemistry of dicyanopyrazine derivatives"

31. 5.84 Dr. A. Haaland (Oslo)
          "Electron diffraction studies of some organo-
          metallic compounds"

11. 6.84[+] Dr. J.B. Street (IBM, California)
          "Conducting polymers derived from pyrroles"

19. 9.84 Dr. C. Brown (IBM, California)
          "New superbase reactions with organic compounds"

21. 9.84[+] Dr. H.W. Gibson (Signal UOP, Illinois)
          "Isomerization of polyacetylene"

19.10.84 Dr. A. Germain (Languedoc, Montpellier)
          "Anodic oxidation of perfluoro organic compounds in
          perfluoroalkane sulphonic acids"

24.10.84[+] Prof. R.K. Harris (Durham)
          "N.M.R. of solids"

28.10.84[+] Dr. R. Snaith (strathclyde)
          "Exploring lithium chemistry: Novel structures, bonding
          and reagents"

7.11.84[+] Prof. W.W. Porterfield (Hampden-Sydney College, U.S.A.)
          "There is no borane chemistry (only geometry)"

7.11.84[+] Dr. H.S. Munro (Durham)
          "New information from ESCA data"

21.11.84[+] Mr. N. Everall (Durham)
          "Picosecond pulsed laser raman spectroscopy"

27.11.84[+] Dr. W.J. Feast (Durham)
          "A plain man's guide to polymeric organic metals"

23.11.84 Dr. T.A. Stephenson (Edinburgh)
          "Some recent studies in platinum metal chemistry "

12.12.84 Dr. K.B. Dillon (Durham)
          "31p N.M.R. studies of some anionic phosphorous
          complexes"

11. 1.85 Emeritus Prof. H. Suschitzky (Salford)
          "Fruitful fissons of benzofuroxanes and isobenzimid-
          azoles (umpolung of o-phenylenediamine)

13. 2.85 Dr. G.W.J. Fleet (Oxford)
          "Synthesis of some alkaloids from carbohydrates"

19. 2.85 Dr. D.J. Mincher (Durham)
          "Stereoselective synthesis of some novel anthracyclin-
          ones related to the anti-cancer drug adriamycin
          and to the steffimycin antibodies"

27. 2.85 Dr. R.E. Mulvey (Durham)
          "Some unusual lithium complexes"

6. 3.85 Dr. P.J. Kocienski (Leeds)
          "Some synthetic applications of silicon-mediated
          annulation reactions"

7. 3.85 Dr. P.J. Rodgers (I.C.I.plc. Agricultural Division,
          Billingham)
          "Industrial polymers from bacteria"

12. 3.85 Prof. K.J. Packer((B.P. Ltd./East Anglia)
          "N.M.R. investigations of the structure of solid polymers

14. 3.85   Prof. A.R. Katritzky F.R.S. (Florida)
"Some adventures in heterocyclic chemistry"

20. 3.85   Dr. M. Poliakoff (Nottingham)
"New methods for detecting organometallic intermed-
iates in solution"

28. 3.85   Prof. H. Ringsdorf (Mainz)
"Polymeric liposomes as models for biomembranes
and cells?"

24. 4.85   Dr. M.C. Grossel (Bedford College, London)
"Hydroxypyridone dyes - bleachable one-dimensional
metals?"

25. 4.85   Major S.A. Shackelford (U.S. Air Force)
"In situ mechanistic studies on condensed phase
thermochemical reaction processes: Deuterium isotope
effects in HMX decomposition, explosives and combustion"

1. 5.85   Dr. D. Parker (I.C.I. plc, Petrochemical and Plastics
Division, Wilton)
"Applications of radioisotopes in industrial research"

7. 5.85   Prof. G.E. Coates (formerly university of Wyoming, U.S.A.)
"Chemical education in England and America: Successes
and deficiencies"

8. 5.85   Prof. D. Tuck (Windsor, Ontario)
"Lower oxidation state chemistry of indium"

3. 5.85   Prof. G. Williams (U.C.W., Aberystwyth)
"Liquid crystalline polymers"

9. 5.85   Prof. R.K. Harris (Durham)
"Chemistry in a spin: Nuclear magnetic resonance"

14. 5.85   Prof. J. Passmore (New Brunswick, U.S.A.)
"The synthesis and characterisation of some novel ^{77}Se
N.M.R. spectroscopy"

15. 5.85   Dr. J.E. Packer (Auckland, New Zealand)
"Studies of free radical reactions in aqueous solution
using ionising radiation"

17. 5.85   Prof. I.D. Brown (McMaster University, Canada)
"Bond valence as a model for inorganic chemistry"

21. 5.85   Dr. D.L.H. Williams (Durham)
"Chemistry in colour"

22. 5.85   Dr. M. Hudlicky (Blacksburg, U.S.A.)
"Preferential elimination of hydrogen fluoride from
vicinal bromofluorocompounds"

22. 5.85   Dr. R. Grimmett (Otago, New Zealand)
"Some aspects of nucleophilic substitution in imidazoles"

4. 6.85   Dr. P.S. Belton (Food Research Institute, Norwich)
"Analytical photoacoustic spectroscopy"

13. 6.85   Dr. D. Woolins (Imperial College , London)
"Metal - sulphur - nitrogen complexes"

14. 6.85   Prof. Z. Rappoport (Hebrew university, Jerusalem)
"The rich mechanistic world of nucleophilic cinylic
substitution"

19. 6.85 Dr. T.N. Mitchell (Dortmund)
"Some synthetic and N.M.R.-spectroscopic studies of
organotin compounds"

26. 6.85 Prof. G. Shaw (Bradford)
"Synthetic studies on imidazole nucleosides and the
antibiotic coformycin"

12. 7.85[+] Dr. K. laali (Hydrocarbon Research Institute, University
of Southern California)
"Recent developments in superacid chemistry and
mechanistic considerations in electrophilic aromatic
substitutions; a progress report"

B. Lectures organised by Durham University Chemical Society
during the period 1982-1985   (+ denotes lectures attended)

14.10.82[+] Mr. F. Shenton (County Analyst, Durham)
"There is death in the pot"

28.10.82 Prof. M.P. Lappert, F.R.S. (Sussex)
"The chemistry of some unusual subvalent compounds
of the main group 1V and V elements"

4.11.82[+] Dr. D.H. Williams (Cambridge)
"Studies on the structures and modes of action of
antibiotics"

11.11.82 Dr. J. Cramp (I.C.I. plc)
"Lasers in industry"
(Joint lecture with the Society of Chemical Industry)

25.11.82[+] Dr. D.H. Richards, P.E.R.M.E. (Ministry of Defence)
"Terminal functional polymers - their synthesis and
uses"

27. 1.83 Prof. D.W.A. Sharp (Glasgow)
"Some radox reactions in fluorine chemistry"

3. 2.83[+] Dr. R. Manning (Dept. Zoology, Durham)
"Molecular mechanisms of hormone action"

10. 2.83 Sir G. Allen, F.R.S. (Unilever Ltd)
"U.K. research"

17. 2.83[+] Prof. A.G. MacDiarmid (Pennsylvania)
"Metallic covalent polymers $(SN)_x$ and $(CH)_x$ and their
derivatives" (R.S.C. Centenary Lecture)

3. 4.83[+] Prof. A.C.T. North (Leeds)
"The use of a computer display system in studying
molecular structures and interactions"

20.10.83[+] Prof. R.B. Cundall (Salford)
"Explosives"

3.11.83[+] Dr. G. Richards (Oxford)
Quatum pharmacology"

10.11.83[+] Prof. J.H. Ridd (U.C.L.)
"Ipso-attack in electrophilic aromatic substitution"

17.11.83[+] Dr. J. Harrison (Sterling Organic)
"Applied chemistry and the pharmaceutical industry"
(Joint lecture with Society of Chemical Industry)

24.11.83[+]   Prof. D.A. King (Liverpool)
"Chemistry in 2-Dimensions"

1.12.83[+]   Dr. J.D. Coyle (The Open University)
"The problem with sunshine"

26. 1. 4[+]   Prof. T.L. Blundell (Birkbeck College, London)
"Biological recognition: Interactions of macromolecular surfaces"

2. 2.84[+]   Prof. N.B.H. Jonathan (Southampton)
"Photoelectron spectroscopy - a radical approach"

16. 2.84[+]   Prof. D. Phillips (The Royal Institution)
"Luminescence and photochemistry - a light entertainment"

23. 2.84[+]   Prof. F.G.A. Stone F.R.S. (Bristol)
"The use of carbene and carbyne groups to synthesise metal clusters"
(The Waddington Memorial Lecture)

1. 3.84[+]   Prof. A.J. Leadbetter (Rutherford Appleton Labs.)
"Liquid crystals"

8. 3.84[+]   Prof. D. Chapman (Royal Free Hospital School of Medicine, London)
"Phospholipids and biomembranes: Basic sciences and future technologies"

28. 3.84   Prof. H. Schmidbaur (Munich, F.R.G.)
"Ylides in coordination sphere of metal: Synthetic, structural and theoretical aspects"
(R.S.C. Centenary Lecture)

18.10.84[+]   Dr. N. Logan (Nottingham)
"N_2O_4 and rocket fuels"

23.10.84[+]   Dr. W.J. Feast (Durham)
"Syntheses of conjugated polymers. How and why?"

8.11.84   Prof. B.J. Aylett (Queen Mary College, London)
"Silicon - dead common or refined?"

15.11.84[+]   Prof. B.T. Golding (Newcastle-upon-Tyne)
"The vitamin B_{12} mystery"

22.11.84[+]   Prof. D.T. Clark (I.C.I., New Science Group)
"Structure, bonding, reactivity and synthesis as revealed by ESCA"
(R.S.C. Tilden Lecture)

29.11.84[+]   Prof. C.J.M. Stirling (University College of North Wales)
"Molecules taking the strain"

6.12.84[+]   Prof. R.D? Chambers (Durham)
"The unusual world of fluorine"

24. 1.85[+]   Dr A.K. Covington (Newcastle-upon-Tyne)
"Chemistry with chips"

31. 1.85[+]   Dr. M.L.H. Green (Oxford)
"Naked atoms and negligee ligands"

7. 2.85   Prof. A. Ledwith (Pilkington Bros.)
"Glass as a high technology material"
(Joint lecture Society of Chemical Industry)

14. 2.85[+]   Dr. J.A. Salthouse (Manchester)
              "Son et lumiere"

21. 2.85[+]   Prof. P.M. Maitlis, F.R.S. (Sheffield)
              "What use is rhodium?"

7. 3.85[+]   Dr. P.W. Atkins (Oxford)
              "Magnetic reactions"

C   Research conferences attended

D   First year induction course, October 1982

This course consists of a series of one hour lectures on the services available in the department.

1. Departmental organisation

2. Safety matters

3. Electrical appliances and infrared spectroscopy

4. Chromatography and microanalysis

5. Atomic absorptiometry and inorganic analysis

6. Library facilities

7. Mass spectrometry

8. Nuclear magnetic resonance spectroscopy

9. Glassblowing technique