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STUDIES ON METAL ALKOXIDES AND CARBOXYLATES FOR USE AS CATALYST PRECURSORS

By

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A thesis submitted to the University of Durham
in candidature for the degree of Doctor of Philosophy

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DECLARATION

The work described in this thesis was carried out in the Chemistry Department of the University of Durham between October 1987 and September 1990. It has not been submitted, either completely or in part, for another degree in this or any other university and is the original work of the author except where acknowledged by reference.

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Studies on Metal Alkoxides and Carboxylates for Use as Catalyst Precursors

Andrew David Keeble B.Sc.

Abstract

This thesis describes research carried out to investigate the feasibility of preparing high activity heterogeneous catalysts from the thermal decomposition of mixed metal alkoxides, carboxylates and hydroxycarboxylates, focusing in particular on the $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst.

The rationale behind the project is discussed in the opening chapter of the thesis which is followed by literature reviews of heterogeneous catalysis and the chemistry of metal alkoxides, carboxylates and hydroxycarboxylates.

Series of co-precipitation/crystallisation reactions of copper and zinc formates, oxalates and adipates were carried out as potential routes to double salts. Some such compounds were formed but in most cases mixtures of the individual salts resulted (xrd).

Thermal decompositions of alkoxides and carboxylates of copper and zinc were investigated both as separate compounds and as mixtures. The nature of volatile species evolved (gas-phase ir) and of the solid residues (microanalysis, xrd) was different for the mixed decompositions compared to the individual ones. The conditions employed in decompositions of copper(II) formate with zinc methoxide (e.g. under vacuum or a stream of N_2 or N_2/H_2) affected the physical nature of the copper metal/zinc oxide residues, smallest particles resulting when using a N_2 stream (transmission electron microscopy). Some of these materials showed activity for methanol synthesis.

The reaction of soluble copper alkoxides (e.g. Cu^IOBu^t) with anhydrous zinc 2-hydroxybenzoate, $Zn(O_2CC_6H_4(OH))_2$, led to the formation of apparently mixed metal compounds, for example $CuZn(O_2CC_6H_4O)_2Py$. The preparation of a new soluble alkoxy derivative of zinc is also reported: $Li_2ZnCl_2(OCH_2CH_2OCH_2CH_2OCH_3)_2$.

A summary of the results of the experimental work is given in relation to the project as a whole.

CONTENTS

Abbreviations and Glossary

OMe = OCH_3

OEt = OCH_2CH_3

OPr^i = $OCH(CH_3)_2$

OBu^t = $OC(CH_3)_3$

Formic acid (methanoic acid) = HCO_2H

Acetic acid (ethanoic acid) = CH_3CO_2H

Oxalic acid (ethanedioic acid) = HO_2CCO_2H

Adipic acid (1,6-hexanedioic acid) =$HO_2C(CH_2)_4CO_2H$

Tartaric acid (2,3-dihydroxybutanedioic acid) = $HO_2CCH(OH)CH(OH)CO_2H$

Salicylic acid (2-hydroxybenzoic acid) $C_6H_4(OH)(CO_2H)$

Py = Pyridine

THF = Tetrahydrofuran.

Discussion of Infra Red Spectra:

s = strong absorption

w = weak absorption

br = broad absorption

sh = shoulder

CHAPTER 1

Introduction

1.1 The Project

The work described in this thesis was carried out to investigate the feasibility of preparing high activity heterogeneous catalysts via the thermal decomposition of metal alkoxides, carboxylates and alkoxycarboxylates.

Typically, heterogeneous catalysts contain two or three metals or metal oxides which need to be suitably dispersed for optimum activity. In particular this project has focused on the $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst, although the work described could be equally well applied to other catalyst systems (e.g. ammonia synthesis).

Methanol is a very important industrial chemical and indeed its importance may increase if its potential as a feedstock or as a fuel is fully exploited[1]. It is currently prepared by passing a high pressure (50-100bar) mixture of carbon monoxide, carbon dioxide and hydrogen (known as synthesis gas or syngas) over a $Cu/ZnO/Al_2O_3$ catalyst at 200-250°C. Formerly methanol was prepared by passing syngas at pressures of 300-350bar over a zinc oxide-chromia catalyst at 380°C which explains why the modern preparation is known as the "low pressure process". The catalyst is currently prepared by the co-precipitation of basic carbonates of the metals concerned at carefully controlled temperature and pH. The precipitate is aged to optimise its structure and is then calcined in air and finally reduced in H_2/N_2 or syngas to produce the active catalyst[2]:

$$\begin{array}{l}\text{Co-precipitated}\\ \text{basic carbonate}\\ Cu_aZn_bAl_c(OH)_x(CO_3)_y\end{array} \xrightarrow[\text{REDUCED}]{\text{AGED, CALCINED}} \begin{array}{l}Cu/ZnO/Al_2O_3\\ \text{Catalyst}\end{array}$$

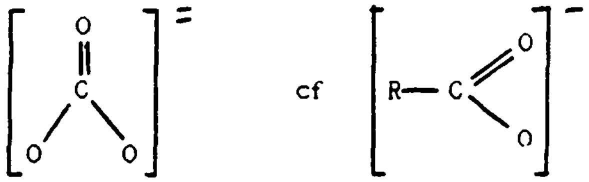
The activity of the catalyst is dependent on several factors including the calcination and reduction conditions employed. However it is the stoichiometry and structure of the hydroxycarbonate precursor which is the prime factor in determining the activity of the catalyst[3]. A problem that arises is that it is not always easy to control the structure and stoichiometry of a co-precipitated solid and therefore catalysts of poor quality may be produced. It was to try and circumvent this problem and perhaps even to exploit the precursor-structure/catalyst-activity relationship that the present work was carried out.

The proposed route for the preparation of catalysts discussed in this thesis involves the calcination and reduction of metal organic compounds (alkoxides, carboxylates and alkoxycarboxylates) of the relevant metals:

$$\underset{Cu_aZn_bAl_c(O)_x(OR)_y(O_2CR)_z}{\text{Metal organic compounds}} \xrightarrow[\text{REDUCE}]{\text{CALCINE}} \underset{\text{Catalyst}}{Cu/ZnO/Al_2O_3}$$

This route has several potential advantages over the traditional co-precipitated basic carbonate route:

(a) the precursors are likely to be molecular species as opposed to the macro-molecular nature of the basic carbonate precursors, which in turn should lead to precursors of more defined structure and more reproducible composition. This is important as the stoichiometry and structure of the precursor is, as already mentioned, crucially important to the activity of the catalyst produced after calcination and reduction. The metal organic species are more likely to have this less complex structure than their basic carbonate counterparts as their coordination is more restricted due to the presence of bulky alkyl groups, e.g. carbonates can coordinate to a metal in any direction whereas the coordination of carboxylates is more limited:



(b) the less compact structure of the precursors should lead to catalysts with more open and thus more active structures.

(c) the stoichiometry and structure of the precursors will be controllable. This means that once a particular system shows promise it should prove possible to adjust the structure of the precursor so as to maximise the activity of the catalyst produced on calcination and reduction. For instance if a precursor contains a formate group then this could be exchanged for an acetate group or if two metals are joined by a dicarboxylate group then by changing the length of the organic chain the metal-metal distance could be varied. This potential ability to control precursor structure is in contrast to the empirical nature of controlling the structure of co-precipitated precursors.

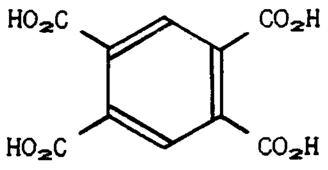
A study of the use of bimetallic alkoxides as potential precursors to methanol synthesis catalysts has previously been carried out[4]. This showed promise as materials were produced which were active catalytically but several problems were encountered:

(a) many of the bimetallic alkoxides were not crystalline - some were liquids others formed glasses;

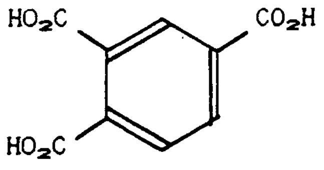
(b) contamination with chlorine (a known poison for copper based catalysts) was common as the syntheses made use of metal chlorides;

(c) the thermal decomposition of the bimetallic alkoxides led to materials which still contained some organic matter.

Other ongoing research is investigating the possibility of using metal salts of aromatic polycarboxylic acids as catalyst precursors[5]. In particular the use of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) and trimellitic acid (1,2,4-benzenetricarboxylic acid) have been investigated as they offer the possibility of coordination to more than one metal in relatively simple symmetric structures and because petrochemical developments suggest increasing availability of these acids.



Pyromellitic Acid



Trimellitic Acid

1.2 The Thesis

The work described in this thesis involves the synthesis and characterisation of suitable precursors, their decomposition under various conditions followed by the evaluation of the materials so produced as catalysts.

The literature surveys in chapters 2 and 3 give background information to the areas of chemistry discussed in this thesis. Chapter 2 discusses the preparation, properties and use of heterogeneous catalysts generally and then goes on to consider the industrial synthesis of methanol by the ICI low pressure process. The preparation of the industrial catalyst is covered as well as mechanisms proposed for the process. Chapter 3 briefly reviews the preparation, properties and uses of metal alkoxides, carboxylates and hydroxycarboxylates

Chapter 4, the first of four experimental chapters, describes attempts at preparing mixed metal salts of copper and zinc by the co-precipitation and co-crystallisation of their formates, oxalates and adipates (1,6-hexanedioates) under various conditions.

Chapters 5 and 6 describe the investigation of thermal decompositions of mixtures of an alkoxide of one metal with a carboxylate of another, with particular attention being paid to zinc methoxide and copper(II) formate. It was expected that this would lead to the production of a mixed metal oxide by loss of methyl formate. Chapter 5 describes the preparation and thermal decomposition of the single components which were carried out to act as controls for the co-decompositions which are described in chapter 6. Chapter 6 also discusses the characterisation and evaluation as catalysts of some of the materials produced.

Chapter 7 discusses the preparation and subsequent reaction of soluble copper alkoxides and zinc hydroxycarboxylates, some of which resulted in the formation of apparently mixed metal systems. Preliminary studies on the impregnation on to alumina extrudate of some of these species followed by their thermal decomposition is described.

Chapter 8 summarizes the work described in the preceding four chapters in relation to the project as a whole. Areas where more work is necessary to clarify some of the observations made together with proposals as to the direction the project should take in the future are discussed.

The references indicated by superscripts throughout the text all appear immediately after chapter 8. Where patents have been referenced the entry in American Chemical Abstracts has been given as well.

An appendix describes experimental techniques and details the various analytical methods used throughout the work.

CHAPTER 2

Heterogeneous Catalysis: Principles and Practice

2.1 Introduction

This chapter serves as a brief introduction to the enormous field of heterogeneous catalysis. It firstly discusses the preparation, properties and characterisation of heterogeneous catalysts in general and then goes on to consider catalysts for the synthesis of methanol in more detail.

2.2 Heterogeneous Catalysis in General[2,6-9]

Catalysts are vital industrial materials without which much of the modern day chemical industry would be redundant, for example the chemistry of syngas (a mixture of carbon oxides and hydrogen) is dictated by catalysts (see Figure 2.1). Indeed it has been claimed[10] that in one way or another they account for some 25% of the gross national product of the USA. Although natural catalysts (e.g. enzymes) have been around for many millions of years, the term "catalyst" is thought to have first been used by Berzelius in 1836 to describe a number of previous observations of enhanced reactions[11].

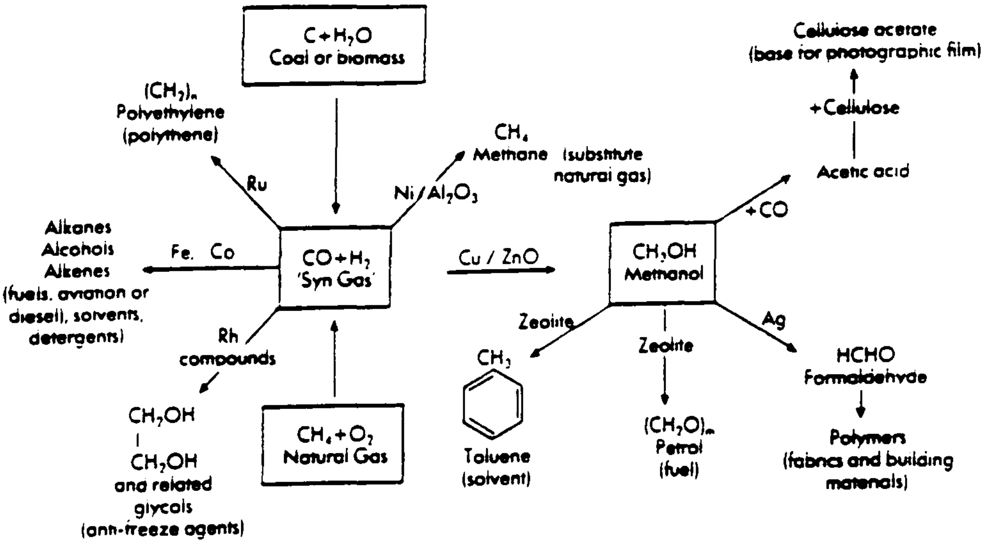


Figure 2.1: The Chemistry of Syngas[10]

The term catalyst is frequently used in everyday language to describe something that brings about a change, but it is difficult to give a precise, chemical, definition of the word. A simple definition, often given, is that a catalyst is something which accelerates a chemical reaction without undergoing an irreversible change in itself. This is a somewhat unsatisfactory description as the properties of all real catalysts do change with use.

Most commercial catalysts are heterogeneous, being metals or alloys usually supported on high area oxides; microporous, microcrystalline aluminosilicates (zeolites); or metal oxides. The term heterogeneous indicates the presence of two or more phases in the catalytic system, usually a solid catalyst and gaseous reactants. This discussion will be limited to such catalysts. Whilst it is not easy to give a concise definition of a heterogeneous catalyst, it is possible to describe the important features of such a catalyst system:

(a) A solid is present which changes the overall rate of a chemical reaction;

(b) The catalyst does not change the position of equilibrium of a reaction. i.e. in principle, the products of the catalysed reaction can be obtained from an uncatalysed reaction under the same conditions, but in practice the uncatalysed reaction may be immeasurably slow or give different products.

(c) The catalyst must have a high productivity: the catalysed reaction steps must occur many times at the active site of the catalyst before activity is lost, meaning that for each tonne of catalyst used many tonnes of product must be formed.

(d) The catalysed reaction steps take place at or very close to the surface of the catalyst, involving gas molecules adsorbed on the surface or involving the topmost atomic layers of the catalyst.

2.2.1 Mode of Action of Heterogeneous Catalysts

A catalyst increases the rate of a chemical reaction as it provides a reaction pathway more energetically favourable than in the uncatalysed reaction (see Figure 2.2). The overall process of a catalytic reaction may be divided into five stages:

(a) transport of reactants to the catalyst;

(b) adsorption of reactants at the catalytically active site;

(c) chemical reactions of adsorbed species (often many steps);

(d) desorption of products from the active site;

(e) transport of the products away from the catalyst.

The overall rate of the reaction may be limited by any of these stages if it is slow. However, in practice, most industrial catalysts are not strongly limited by any one stage in particular.

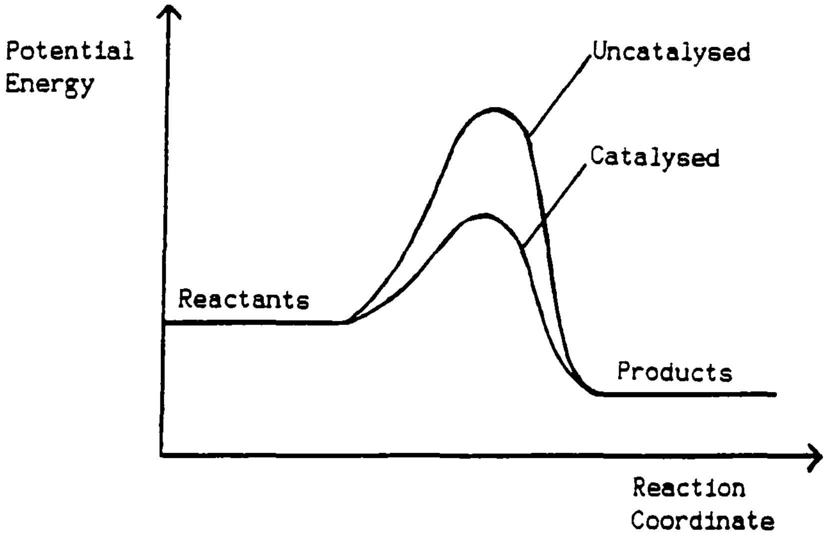


Figure 2.2: Energy Profiles of Catalysed and Uncatalysed Reactions

The adsorption of a reactant on to a surface can occur in several ways. The strength of this adsorption is important as if it is too strong it will be correspondingly difficult to remove the product and indeed it may even constitute a poison, whilst if it is too weakly adsorbed it will not remain on the surface long enough to react. There are three ways in which adsorption can occur: physical adsorption (or physisorption); associative chemical adsorption and dissociative chemical adsorption (both termed chemisorption). These are discussed below using the interaction of carbon monoxide with various metals as an example (see Figure 2.3).

Physisorption involves no special bonds being formed between the gas and the surface and no breaking of bonds or any significant changes in bond energies in the reactant molecule. It is a low energy adsorption, being extensive only at low temperatures. It is, however, frequently important as it can act as a precursor to chemisorption. An example is the interaction of carbon monoxide and αAl_2O_3.

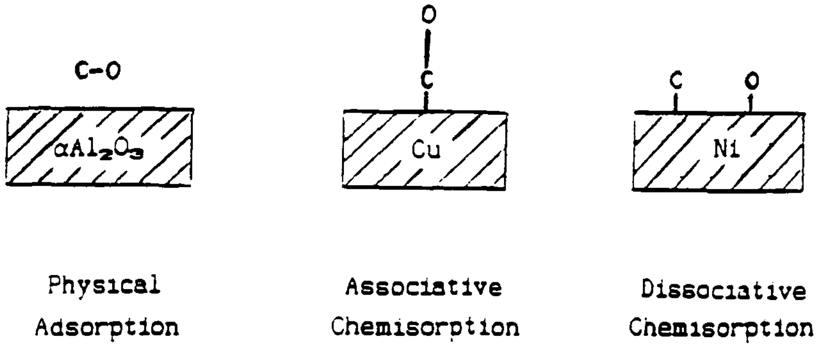


Figure 2.3: Schematic Diagram of the Adsorption of Carbon Monoxide on Various Surfaces

Associative chemisorption involves the formation of a stronger interaction between the adsorbed molecule and the surface than with physisorption. Although no bonds are broken in the adsorbed molecule, they are weakened, and unlike physisorption this effect is dependent on both the gas and the solid surface. An example is the chemisorption of carbon monoxide on to copper, which occurs in methanol synthesis, where it is important that the C-O bond is not broken as this could lead to the production of methane and water.

Dissociative chemisorption is similar to associative chemisorption, except that in this case a bond is broken in the adsorbed molecule. It is thought that an, associatively chemisorbed, intermediate may be formed before the adsorbed molecule dissociates. Dissociative chemisorption is also very much dependent on the nature of the solid and the gas. Examples are the chemisorption of hydrogen on to copper or nickel to give adsorbed hydrogen atoms and the chemisorption of carbon monoxide on to nickel to give adsorbed carbon and oxygen. The latter is utilised in the catalysis of the methanation of carbon monoxide in, for example, the synthesis of substitute natural gas from coal or oil, where it is essential that the C-O bond is broken.

2.2.2 Essential Properties of Heterogeneous Catalysts

The requirements of modern day catalysts are many and varied, but there are three main attributes that a material must have in order to be regarded as a good catalyst:

(a) Activity:

The activity of a catalyst is a measure of its ability to convert reactants into products. For a given system it is generally dependent on the surface area of the active constituent of the catalyst, so this is usually maximised in the preparation of the catalyst. It can be expressed in several forms:

kg reactant converted per kg catalyst per hour;

percentage change in reactant (conversion);

number of molecules reacting per second per active site (turnover number).

(b) Selectivity:

The selectivity of a catalyst is a measure of its ability to give the desired product out of all possible products and is as important as good activity in assessing the performance of a catalyst. A catalyst will have a good selectivity if it greatly increases the rate of reaction leading to the desired product whilst not increasing the rates of competing reactions. It is usually expressed as amount of product as a percentage of the amount of reactant converted.

(c) Life:

The life of a catalyst is the time for which the catalyst keeps a sufficient level of activity and/or selectivity. The lifetime of a methanol synthesis catalyst is about 5 years whilst that for ammonia synthesis is about 8 years. There are three causes of catalyst decay: physical causes, poisoning by impurities, and poisoning by reactants or products.

The physical causes of catalyst decay may be on micro- or macro-scale. The sintering or aggregation of the small metal crystallites lead to a loss in surface area and thus activity, whilst the break up of catalyst pellets will hinder gas flow through the catalyst bed thus decreasing the output. Both of these types of failure, if severe, may limit the performance of the plant to such an extent that a shutdown and catalyst change is required. However it should be noted that commercial catalysts are designed with these factors in mind so sintering is usually slow as the active species is supported on a stable oxide and the catalysts are made with sufficient strength to withstand the stresses of normal plant operation.

Impurities in the feed or catalyst may affect the active sites of a catalyst, a phenomenon known as poisoning. This can lead to the loss of activity if the poison deactivates an active site, or a loss of selectivity as well if the poison modifies an active site so as to alter the relative rates of different reactions. Examples of poisons are chlorine and sulphur for copper-based catalysts or arsenic for nickel-based catalysts which are all examples of irreversible poisoning. Some types of poisoning are termed reversible as the poison is not too strongly chemisorbed and no reconstruction of the active site has taken place so that the poison may be removed. An example of this is the poisoning caused by traces of carbon dioxide and water in ammonia synthesis which leads to the formation of adsorbed oxygen on the iron surface which then prevents nitrogen adsorption. This poisoning is reversed by reduction with hydrogen which returns the surface to its original state. It should be noted that gross oxidation with oxygen would give bulk changes which cannot easily be reversed.

Poisoning may also result from the formation on catalysts of carbonaceous deposits, usually described as coke despite the fact that they contain hydrogen. These are formed from the organic reactants and products of the reaction. Coking is the most common form of poisoning caused by reactants or products, but there are others, for example, any iron in a methanol synthesis catalyst may promote Fischer-Tropsch reactions leading to blocking of the catalyst by waxes.

(d) Other Properties:

Whilst the attributes of activity, selectivity and life are the most important in the evaluation of a material as a catalyst there are other considerations. The physical properties of catalysts are important in that a catalyst consisting of very small crystallites, whilst having a huge surface area and thus, a potentially very good activity, would be of limited use as a catalyst as a very large pressure would be required to force the reactant gases through the catalyst bed. It is also essential that there is a good, even, flow of gas through the reactor so as to avoid thermal hotspots in the catalyst bed which would in turn lead to sintering. It is for these reasons that most catalysts are pelleted. There are various forms of pellet with typical sizes ranging from 3-20mm. The cost of a catalyst is also important, as although they have a high productivity, they are valuable commodities. Clearly a catalyst which is more expensive to make or use would have to outperform a cheaper competitor to a sufficient degree to compensate for the increased cost.

2.2.3 Preparation of Heterogeneous Catalysts

The successful preparation of catalysts necessarily involves producing materials which satisfy the above criteria. The following section gives a broad outline of the various methods that are used, but it should be noted that attention to detail in catalyst manufacture is vital, as small changes in procedure can lead to large effects on catalyst performance. It is for this reason that much of the detail of the commercial manufacture of catalysts is not in the open literature.

(a) Unsupported Metals

As previously stated most metal based catalysts require a large surface area which is usually maintained by spreading the metal over an oxide support. There are, however, some reactions where the rate of the catalysed reaction is so fast that a high surface area is not required and thus an unsupported metal may be used. The most common example of this is the precious metal gauze used for example, in the oxidation of ammonia in nitric acid plants. The gauze, usually made from a platinum-rhodium alloy is woven up to three metres in diameter with the individual strands of metal being only about 50 microns in diameter.

(b) Catalysts Prepared by Fusion

The fusion of metals or their oxides is not widely used in the manufacture of catalysts as, although it gives excellent scope for the mixing of the components, it leads to low surface area materials. These then require activation, by the removal of some component, to generate porosity and thus activity which is not always possible. However the ammonia synthesis catalyst is made in this way.

(c) Wet Methods

This is the most commonly used method to manufacture industrial catalysts. There are two principal methods used: impregnation, where the active component is placed on to a preformed support; and co-precipitation, where the active phase and support are made together. The choice of method is dependent on the properties required of the catalyst. The precipitation method tends to give a higher concentration of the active phase than with impregnation, but can lead to a poor mechanical strength. Impregnation, however can make use of preformed refractory supports which tend to make impregnated catalysts useful in high temperature processes. Sometimes the processes are combined with a precipitated catalyst then being impregnated with a promoter. The methanol synthesis catalyst is made by a co-precipitation method (see later) whilst the nickel-based steam-reforming catalyst is made by impregnation, so that it can withstand the high operating temperatures (typically 800°C) of the process.

These methods produce precursors, the stoichiometry and structure of which determine how good a catalyst they will make.

These are then calcined and reduced to produce the active catalyst. These stages are also important as if the conditions employed are too harsh then an inactive catalyst will result from, for example, sintering of the active metal.

2.2.4 Characterisation and Evaluation of Heterogeneous Catalysts

Many of the characteristics of a good catalyst have already been discussed. The measurement of these properties whilst very important, is not always straightforward. A problem that still remains, despite great advances in the measurement techniques, is that it is not yet possible to make all such measurements on a working catalyst. There are numerous techniques that are used to evaluate the performance of a catalyst a summary of which is given below.

The bulk chemical properties of a catalyst are determined mainly by elemental analysis (indicating levels of any impurities), x-ray diffraction (indicating phases present) and electron microscopy (indicating particle size). Indeed, electron microscopy is also useful in determining the elemental analysis and crystal structures of particles present.

The surface chemical properties of a catalyst system are important as heterogeneous catalysis is a surface phenomenon. A wide range of surface techniques is used to determine various properties, for example: Photoelectron spectroscopy, PES, Auger spectroscopy, AES, and secondary ion mass spectroscopy, SIMS (chemical identity of surface layers); Temperature programmed desorption, TPD (chemical identity of adsorbed species); Physisorption of gases, usually nitrogen (total surface area); Chemisorption of gases, usually carbon monoxide, hydrogen or oxygen, and surface reaction of nitrous oxide (surface area of metal components); Extended x-ray absorption fine-structure analysis, EXAFS (atomic structure of surfaces and adsorbates).

The physical properties of catalysts are also important. These include the strength and the pore structure of the catalyst particles. The size and accessibility of pores is important as they determine how easily reactant gases may travel to active sites and they are assessed using mercury porosimetry.

Once the catalyst has been through and satisfied the relevant criteria of the above tests, its actual performance as a catalyst must be assessed. The initial evaluation is caried out in a microreactor, commonly a stainless steel tube loaded with catalyst (usually 1-5ml), through which reactant gases are fed at pressures of up to about 50bar. The exhaust gases are analysed by gas chromatography or by mass spectroscopy and thus a measure of activity may be obtained. If the activity is satisfactory, studies on lifetime and poisons are then made. The next stage is that of a semi-technical test where a larger volume of catalyst (100-1000ml) is assessed over a longer period of time. Then and only then can a catalyst be considered for use in a full scale plant.

2.3 Catalysis of Methanol Synthesis[2,12]

The above section deals with the preparation, characterisation and evaluation of catalysts in general. There now follows a more detailed account of the chemistry of methanol synthesis catalysis which also serves to expand some of the issues raised above.

2.3.1 The Industrial Manufacture of Methanol

The synthesis of methanol from the hydrogenation of carbon monoxide and carbon dioxide (syngas) is of major industrial importance. The main reactions involved are:

$CO + 2H_2 \longrightarrow CH_3OH$ $\Delta H^{\circ}_{298}=-90.6 kJmol^{-1}$, $\Delta G^{\circ}_{298}=-25.3 kJmol^{-1}$

$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$ $\Delta H^{\circ}_{298}=-49.5 kJmol^{-1}$, $\Delta G^{\circ}_{298}= +3.3 kJmol^{-1}$

$CO + H_2O \longrightarrow CO_2 + H_2$ $\Delta H^{\circ}_{298}=-41.2 kJmol^{-1}$, $\Delta G^{\circ}_{298}=-28.6 kJmol^{-1}$

The last two reactions combined are equivalent to the first so methanol may be made from either of the carbon oxides present in syngas. This point is discussed later when the mechanism is considered.

Methanol is one of the least thermodynamically prefered products of the hydrogenation of carbon oxides, the formation of higher alcohols and hydrocarbons being favoured. Therefore a highly selective catalyst is essential if methanol is to be made in this way. The first catalysts used, the so called high pressure catalysts, consisted of ZnO/Cr_2O_3 and necessitated the use of high temperatures (380°C) and pressures (300 bar). These were superseded in the 1960's by the low pressure catalysts consisting of copper, zinc oxide and either alumina or chromia (see later).

The modern low pressure methanol plants operate at pressures of 50-100 bar and temperatures of 200-250°C. A flow chart of such a plant is shown in Figure 2.4. It is based on the steam reforming of natural gas which is the usual source of syngas. The process involves the continuous circulation of syngas through the converter with the methanol being removed by condensation and the pressure of the system being maintained by the continuous addition of syngas. The crude methanol contaminated with water and higher alcohols is purified by distillation. The low conversion per pass over the catalyst and the recycling of the unreacted gas enables the temperature of the catalyst bed to be controlled. However the highly exothermic nature of the reaction means that special types of reactor have to be used. Typically a Quench reactor is used, which controls the temperature as only part of the circulating gas is preheated before being fed into the reactor, the rest of the gas (at ambient temperature) is injected at various intervals along the reactor thus moderating the temperature.

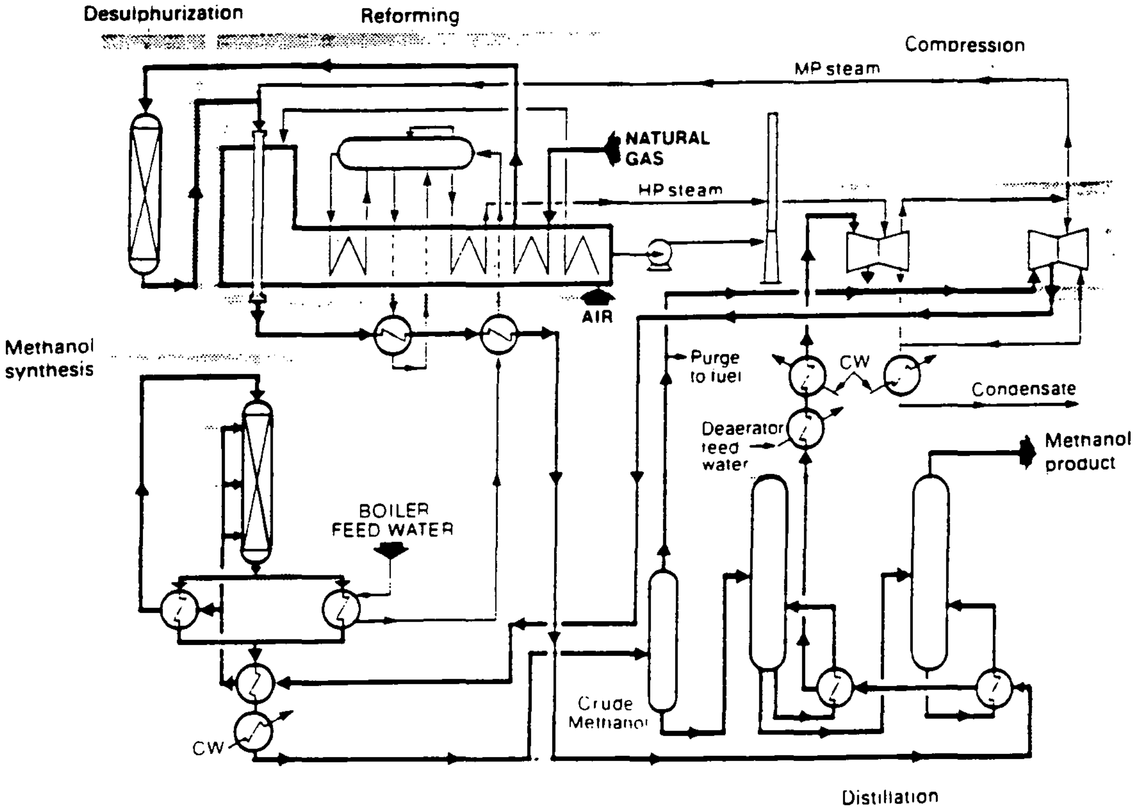


Figure 2.4: Flowsheet of a Typical Low Pressure Methanol Plant[2]

2.3.2 Preparation of Methanol Synthesis Catalysts

The Cu/ZnO/Al_2O_3 ICI low pressure methanol synthesis catalyst is made by a coprecipitation method. The development of the catalyst to its present state has taken many years of often empirical experimentation. Indeed it has evolved from a one stage precipitation[13], to a two stage precipitation (first aluminium and zinc, followed by copper and zinc)[14], and finally to a multi-stage precipitation[15]

The precipitations involve the continuous mixing of solutions of the metal nitrates concerned with a solution of sodium carbonate. The pH of the mixture is maintained at pH7 as otherwise the stoichiometry and also particle size of the precipitate changes (see Figure 2.5).

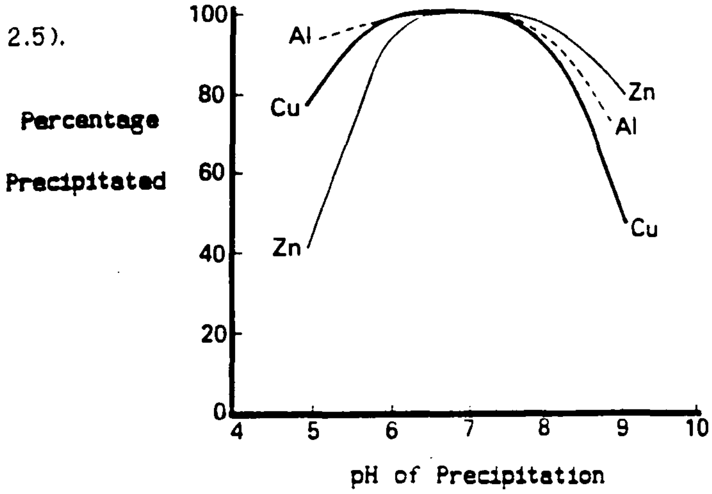


Figure 2.5: Variation With pH of the Composition of Cu/ZnO/Al_2O_3 Catalysts Prepared by Precipitation[2]

The precipitate is then aged to obtain the optimum chemical and physical state of the precursor. Washing is required to remove, for example, sodium which can adsorb to the high surface area of the material. The use of nitrates, hydroxides and carbonates in the precipitations removes the possibility of poisons (e.g. sulphur) being formed during the calcination of the precursor.

The calcined precursor which consists of the oxides of the metals is made into pellets and only activated, in a hydrogen stream, once it is inside the reactor. This is because the catalyst once activated is very sensitive to air and is thus not easily transported.

The fact that the stoichiometry and structure of the methanol synthesis catalyst precursor is so crucial to the activity of the actual catalyst has lead to much work in this area. The work has tended to focus on the copper and zinc components of the catalyst as the alumina is generally considered to act as a support and not to have any catalytic effect on the reaction[16]. The co-precipitation of copper and zinc hydroxycarbonates (Cu:Zn ratio, 2:1) has been shown to give a two phase system containing malachite and aurichalcite[3,17,18]. The amounts of each phase present were estimated by quantitative x-ray diffraction. The effect of ageing (stirring in the mother liquor at 60°C) on the structure of the precursor and on the activity of the catalyst once produced have been investigated[3]. It was found that ageing led to the rapid disappearance of the aurichalcite phase with the production of a mature, copper enriched malachite phase. In addition to this, the activity of the catalysts derived from precursors aged for thirty minutes or more were much higher than those derived from unaged precursors. Therefore it appears that the formation of the malachite phase is essential if an active catalyst is to be produced.

The $Cu/ZnO/Al_2O_3$ catalyst system is not the only system that has been investigated with regard to methanol synthesis. Two novel routes to a supported copper-based catalyst have been reported. The first involves the formation of Raney copper by leaching ternary copper/zinc/aluminium alloys with strong aqueous solutions of sodium hydroxide[19-22]. The catalysts so produced have activities comparable to the industrial catalyst with a small (2%) residual amount of zinc and aluminium being present. The second involves the careful oxidation of suitable intermetallic compounds. The thorium/copper compounds, $ThCu_6$, $ThCu_{3.6}$, $ThCu_2$ and Th_2Cu all react with synthesis gas to give a thoria-supported copper catalyst which is extremely active for methanol synthesis[23,24]. Following these observations the use of alloys of copper with metals that were easier to handle (non-radioactive), for example cerium and neodymium were investigated[25,26]. In these cases very good activities were observed for methanol synthesis at temperatures as low as 70°C (industrial plant operates at 200-250°C). These catalysts although very active were not suitable for use on a large scale because of the engineering problems associated with the large increase of volume of the catalyst on oxidation of the metal alloys.

2.3.3 The Methanol Synthesis Reaction Mechanism

The mechanism of the synthesis of methanol from carbon monoxide, carbon dioxide and hydrogen over $Cu/ZnO/Al_2O_3$ catalysts has been the subject of much study, the results of which are often conflicting. As previously stated the role of the alumina is thought by most workers to be that of a mechanical support. The roles of copper and zinc oxide and whether methanol is made from carbon monoxide or carbon dioxide are still uncertain.

One view is that the active site is Cu(I) dispersed in ZnO[16,27]. The chemisorption of carbon monoxide on these sites, being energetically more favourable than on Cu(0) or Cu(II), was thought to be of primary importance in the synthesis of methanol. This proposal has been challenged, but some recent work has supported this viewpoint[28].

The view of other workers, notably those at ICI, is that methanol is synthesised from the hydrogenation of carbon dioxide on a Cu(0) site[29]. This stems from much detailed work including radiolabelling experiments[1,30] and work which shows that methanol synthesis activity is linearly related to the surface area of exposed copper[31,32]. The proposed mechanism is that carbon dioxide and hydrogen coadsorb on to a metallic copper site to give a surface formate species which is then reduced to give methanol. Carbon monoxide is required to reduce the surface oxide so formed to copper metal, producing carbon dioxide, and thus a cycle is formed (see Figure 2.6). However no specific chemical role for the zinc oxide was identified which other workers claim has a large synergic effect[33,34]. A more recent study has suggested that the zinc oxide may act so as to promote the activation of carbon dioxide[35] and to act as a store of adsorbed hydrogen which may explain the observed synergy, denied by the ICI workers[29].

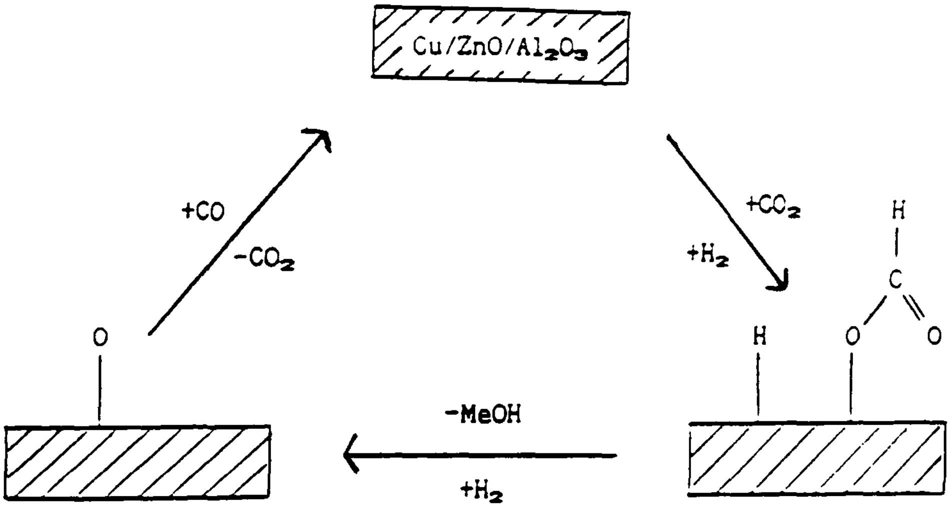


Figure 2.6: Proposed Mechanism for the Synthesis of Methanol from Syngas Over Cu/ZnO/Al_2O_3

A third view, yet to gain much support, is that minute Schottky junctions at the interface between copper metal and zinc oxide in the catalyst affect the surface chemistry of the system thus leading to the catalytic effect. This theory supports the proposed synergy between copper and zinc oxide and claims that it is due to the perturbation of the oxide defect equilibria by the metal/oxide junctions in the catalyst. This in turn leads to a large increase in the number of oxide vacancies on the catalyst surface which are proposed as the active site[36].

The reasons for the controversy over the mechanism, which looks likely to continue for some time, are many: the complexity of the catalyst system is greater than other heterogeneous catalysts; the properties of the catalysts are highly dependent on details, often very minor, of their preparation and so it is not unknown for catalysts of the same nominal composition but made in different ways to have markedly different activities; the nature of the catalyst varies with reaction conditions so investigations carried out under conditions far removed from those of the industrial synthesis are of uncertain relevance to it; poisoning is a more common problem on a lab scale than on an industrial scale. However for a better understanding of the catalyst system, and thus for the design of better catalysts, it is essential that the question of mechanism is resolved.

2.4 Summary

The above brief discussion of heterogeneous catalysis shows how important such materials are in the chemical industry, and thus in everyday life. The complexity of systems involving heterogeneous catalysts is enormous and whilst our understanding of them is improving many questions remain unanswered. It is important to note that minor alterations in the synthesis of catalysts can lead to the production of catalysts with markedly different activities.

CHAPTER 3

Preparation, Properties and Uses of Metal Alkoxides, Carboxylates and Hydroxycarboxylates

3.1 Introduction

This chapter gives a brief introduction to the general chemistry of metal alkoxides, carboxylates and hydroxycarboxylates. It firstly discusses alkoxides before going on to carboxylates and hydroxycarboxylates. In each section the preparation, properties and uses of the compounds are discussed.

3.2. Alkoxides

Metal alkoxides are compounds in which metal atoms are attached to alkyl groups through oxygen atoms. Metal aryloxides are related species which have aryl groups attached to metals through oxygen atoms. Metal alkoxides can be considered as derivatives of either alcohols, where the acidic hydrogen is replaced by a metal, or as derivatives of metal hydroxides, where the hydrogens have been replaced by alkyl groups:

$$n(RO{-}H) \longrightarrow M(O{-}R)_n \longleftarrow M(O{-}H)_n$$

3.2.1 Preparation of Alkoxides

There are a large number of synthetic routes to metal alkoxides, some of which are more suited to particular metals or alkoxy groups than others. The following section reviews the available methods[37,38].

(a) From the Metal and Alcohol

The direct reaction between an alcohol and a metal provides the simplest preparative route to alkoxides:

$$2M + 2nROH \longrightarrow 2M(OR)_n + nH_2$$

However, the relatively low acidity of alcohols limits this method to the more electropositive metals. For Group I metals the reaction is spontaneous and exothermic and can be used to prepare the pure alkoxides[39,40], e.g.

$$2Na + 2CH_3CH_2OH \longrightarrow 2Na(OCH_2CH_3) + H_2$$

The reaction rate is, however, very dependent on the alcohol with the more sterically hindered (and less acidic) tert-butanol reacting much more slowly than methanol with sodium or lithium. Heating is required in some cases.

Less electropositive metals, such as those of Group II and aluminium, do not readily react with alcohols. In the case of aluminium and phenol, reaction occurs under reflux if the oxide coat on the aluminium is mechanically removed[41]. However if an initiator, such as iodine or mercury(II) chloride is used then other metal alkoxides may be prepared in this manner. The mode of action of such materials is unclear, possibilities being that they act so as to clean the metal surface or that they form intermediate halide derivatives which then undergo facile reaction with the alcohol. e.g.[42]

$$Mg + 2ROH \xrightarrow{I_2} Mg(OR)_2 + H_2$$

There are other more complex ways of preparing metal alkoxides from the reaction between alcohols and metals. One such, which has been used to prepare copper(II) alkoxides[43,44], and alkoxides of other transition metals (e.g. titanium, scandium, zirconium, niobium and tantalum)[45] is the anodic dissolution of the metal into alcohols containing conducting electrolytes. This method (originally demonstrated in 1906[46]) has been used to prepare copper(II) methoxide, ethoxide, propoxide and butoxide[43] by the electrolysis of a solution of the parent alcohol and tetrabutylammonium chloride in N,N-dimethylformamide with a platinum cathode and a copper anode.

(b) From the Metal Halide

There are several different methods of preparing metal alkoxides starting with a metal halide. The combination of these methods means that metal halides are the most useful and exploited of the starting materials from which to make metal alkoxides.

(i) The direct reaction of metal halides with alcohols provides the most straightforward preparative route. However the reactions only go to completion for less electropositive elements such as boron, silicon and phosphorus (i.e for those halides readily hydrolysed by water). e.g.[47]

$$SiCl_4 + 4EtOH \longrightarrow Si(OEt)_4 + 4HCl$$

In the case of the more electropositive metals, direct reaction leads to alcohol adducts or to the partial replacement of halide ligands. e.g.[47]

$$TiCl_4 + 3EtOH \longrightarrow TiCl_2(OEt)_2.EtOH + 2HCl$$

The phenoxides are formed more readily due to the higher acidity of phenol when compared to that of aliphatic alcohols. For example titanium phenoxide is formed by the reaction of phenol with titanium(IV) chloride in benzene[48]:

$$TiCl_4 + 4PhOH \longrightarrow Ti(OPh)_4 + 4HCl$$

(ii) The addition of a base to the reaction mixture of metal halide and alcohol may facilitate the formation of alkoxides in cases where the direct reaction leads to the formation of chloro-alkoxides. For example, soluble titanium alkoxides may be made by the reaction of titanium(IV) chloride and an alcohol in the presence of ammonia. The ammonia removes the hydrogen chloride from the reaction mixture as it leads to the precipitation of ammonium chloride in solvents such as benzene[49].

$$TiCl_4 + 4ROH + 4NH_3 \longrightarrow Ti(OR)_4 + 4NH_4Cl$$

The possible reaction between the alcohol and liberated hydrogen chloride to form a mixture of organic compounds and water leads to complications in "(i)" above. This is especially true for tertiary alcohols[50] and indeed tertiary alkoxides of titanium and zirconium were only obtained if pyridine was added to a mixture of the metal chloride and the alcohol followed by the addition of ammonia[51]. The pyridine, by forming pyridinium chloride, inhibits any side reaction of the hydrogen chloride with the alcohol.

(iii) A third method of preparing alkoxides using metal halides as the starting material involves their reaction with alkali metal alkoxides. A large number of alkoxides may be made in this manner. e.g.[52]

$$WCl_5 + 5Na(OEt) \longrightarrow W(OEt)_5 + 5NaCl$$

However, despite the usefulness of this method there are two major drawbacks. Firstly, double alkoxides are sometimes formed, for example tin forms double alkoxides with sodium rather than the desired single alkoxide[53]:

$$2SnCl_4 + 9Na(OEt) \longrightarrow NaSn_2(OEt)_9 + 8NaCl$$

Secondly, some alkoxides form complexes with lithium chloride, for example although zinc methoxide and iso-propoxide may be precipitated by the reaction of the lithium alkoxide and zinc chloride in the parent alcohol, zinc ethoxide is not. Instead the reaction between lithium ethoxide and zinc chloride in ethanol leads to the formation of a soluble complex[54]. Indeed a similar problem was encountered during the course of the present study in the attempted preparation of zinc 2-(2-methoxyethoxy)ethoxide: the reaction of the lithium alkoxide with zinc chloride led to the precipitation of a complex rather than the formation of the desired soluble alkoxide (see chapter 7).

(c) Exchange Reactions

(i) A large number of metal alkoxides have been made by alcohol exchange reactions:

$$M(OR)_n + xR'OH \longrightarrow M(OR)_{n-x}(OR')_x + xROH$$

The degree of exchange is governed by several factors: the nature of the alkoxy group is important - generally tertiary groups are more readily replaced than secondary groups and secondary groups are more readily replaced than primary groups. However another factor is the volatility of the alcohols concerned. If the alcohol which is formed during the exchange reaction can be continuously removed by distillation (usually as an azeotrope), then it is possible to reverse the above order. e.g.[54]

$$Zn(OMe)_2 + 2Pr^iOH \longrightarrow Zn(OPr^i)_2 + 2MeOH$$

However this can also allow partial exchange of the alcohol. e.g.[55]

$$Ta(OMe)_5 + 4Bu^tOH \longrightarrow Ta(OMe)(OBu^t)_4 + 4MeOH$$

Alcohol exchange reactions are particularly useful for the synthesis of phenoxides because phenols are more acidic and less volatile than alcohols. e.g.[56]

$$Zr(OPr^i)_4 + 5PhOH \longrightarrow Zr(OPh)_4.PhOH + 4Pr^iOH$$

(ii) A second type of reaction involving an exchange reaction of an alkoxide is that of transesterification. The reaction of an ester with an alkoxide leads to the formation of an equilibrium[57]:

$$M(OR)_n + xCH_3COOR' \rightleftharpoons M(OR)_{n-x}(OR')_x + xCH_3COOR$$

The position of the equilibrium may be displaced so that a new alkoxide would be formed if the ester so produced is more volatile than the original ester allowing it to fractionated out of the reaction mixture. This method has been used to prepare tert-butoxides of, for example, titanium, zirconium and hafnium which could not be made via alcohol exchange reactions[58].

(d) Other Methods

Examples of some of the other methods used to prepare alkoxides are given below.

Alkyl groups attached to metals may be cleaved in a stepwise manner by reaction with alcohols to yield alkoxides. It is possible to isolate some of the intermediate alkyl alkoxides. e.g.[59,60]

$$ZnR_2 + MeOH \longrightarrow RZnOMe + RH$$

$$RZnOMe + MeOH \longrightarrow Zn(OMe)_2 + RH$$

The reaction of metal hydroxides and oxides with alcohols leads to the formation of alkoxides. It is essential that the water that is produced is continuously removed, usually as an azeotrope, by fractionation. This method has been used to prepare alkali metal alkoxides. e.g.[61]

$$NaOH + EtOH \longrightarrow NaOEt + H_2O$$

The reaction of metal dialkylamides with alcohols to form alkoxides is particularly useful in the synthesis of alkoxides of early transition metals. The dialkylamines evolved are readily removed in vacuo due to their high volatility, thus providing a useful synthetic pathway to some alkoxides which are otherwise difficult to prepare. e.g.[62]

$$Zr(NEt_2)_4 + 4Bu^tOH \longrightarrow Zr(OBu^t)_4 + 4HNEt_2$$

3.2.2 Structural Properties of Alkoxides

Alkoxides have physical properties that vary according to the nature of the metal and alkoxy group. They range from non-volatile, insoluble solids (e.g. copper and zinc dialkoxides) to volatile, soluble solids (e.g. titanium and zirconium tetraalkoxides). This great variation in physical properties is due to the differing molecular complexities observed in alkoxide chemistry: those forming large polymeric frameworks are insoluble and non-volatile whilst those forming small oligomers are generally volatile and soluble.

The formation of oligomers or larger polymeric frameworks is due to alkoxide groups bridging two or more metal centres (i.e. acting as μ_2, μ_3, μ_4 ligands) and the tendency of metals to increase their coordination number. The extent of oligomerisation is affected by:

(a) The Alkoxy Group: For a given metal the more bulky the alkoxy group, the lower the degree of association. This steric effect is demonstrated by the insoluble, non-volatile, polymeric nature of aluminium methoxide compared to the volatile, soluble, tetrameric nature of aluminium iso-propoxide[63].

(b) The Metal: The oxidation state of the metal determines the number of alkoxy groups present per metal which in turn affects the bridging: those of low oxidation state requiring more bridges to achieve a given coordination number than those of higher oxidation state. The size of the metal may also affect the degree of bridging as the larger the size of the metal atom, the more easily it can accomodate bulky alkoxy groups and therefore the more easily it can increase its coordination number. This effect is seen in the molecular complexities of titanium and zirconium alkoxides: for a given substituent the molecular complexity is higher for the zirconium alkoxide[64,65].

The simple alkoxides of copper and zinc are insoluble , non-volatile solids due to their highly polymeric nature[54,66,67] so it has not been possible to obtain crystals for x-ray structure determination. Structures have been postulated for copper(II) methoxide with some authors suggesting the copper is six coordinate in a distorted octahedral environment[66] whilst others prefer a linear chain model with the copper being four coordinate[68] similar to that observed for copper(II) chloride[69].

The soluble, volatile nature of more complex copper alkoxides, for example copper(I) tert-butoxide[70], has enabled x-ray crystal structures to be determined. Copper(I) tert-butoxide was found to consist of planar, tetrameric rings with the copper being two coordinate and the alkoxy groups acting as μ_2 ligands (see Fig 3.1)[71]. This structure is thought to be favoured over the more common cubane structure with its μ_3 alkoxy ligands observed for thallium(I) methoxide[72] and the tert-butoxides of potassium, rubidium and cesium[73] (see Fig 3.2) as it enables the Cu^I to have essentially linear O-Cu-O coordination. A cubane structure is also observed for methylzinc methoxide: MeZnOMe[74].

The simple alkoxides of aluminium are, at least to some extent, soluble volatile species[75]. A crystal structure of aluminium isopropoxide showed it to contain tetrameric units (see Fig 3.3)[63]. These tertramers contain two different types of aluminium and alkoxy groups: a central aluminium atom is six coordinate in an octahedral environment whilst the other three aluminium atoms are four coordinate in tetrahedral environments; six of the alkoxy groups are terminal (μ_1) whilst the other six bridge between aluminium atoms (μ_2). It is interesting to note that after distillation aluminium isopropoxide consists of predominantly trimeric units, it is only after a period of days that these "age" to the tetramers observed in the crystal structure.

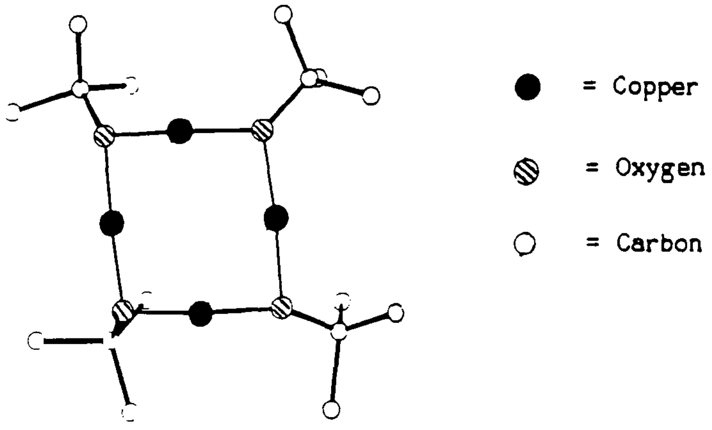


Figure 3.1: Crystal Structure of Copper(I) tert-Butoxide[71]

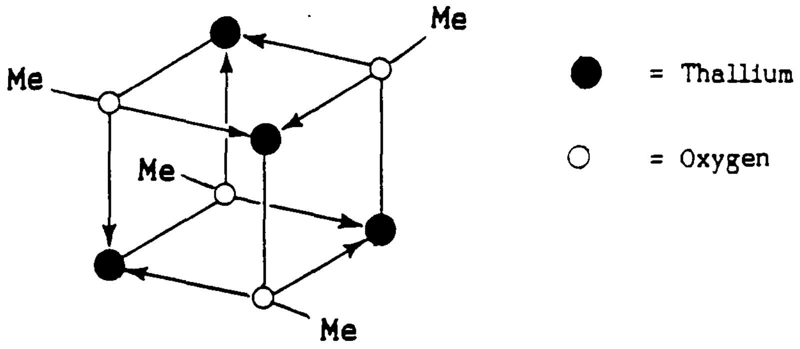


Figure 3.2: Crystal Structure of Thallium(I) Methoxide[72]

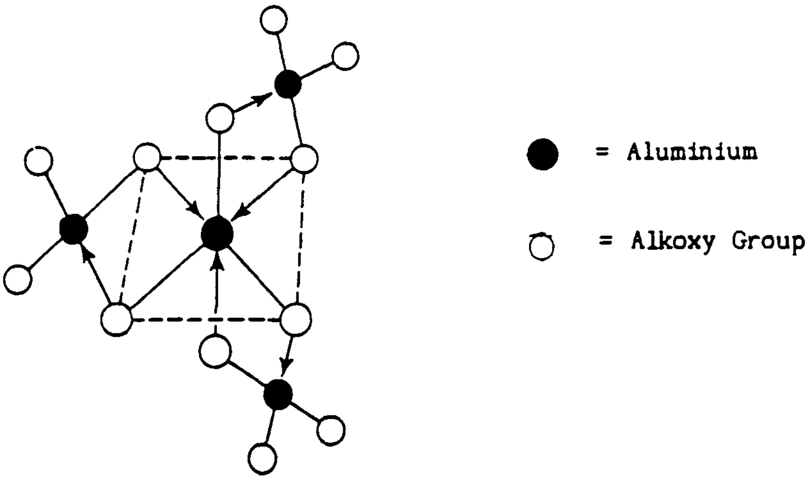


Figure 3.3: Crystal Structure of Aluminium iso-Propoxide[73]

3.2.3 Reactions of Alkoxides

Metal alkoxides are generally very reactive species and the following section gives a summary of their more important reactions.

(a) Hydrolysis

Metal alkoxides are rapidly hydrolysed leading to the formation of hydroxides or hydrated oxides. e.g.

$$Al(OR)_3 + 3H_2O \longrightarrow Al(OH)_3 + 3ROH$$

This means that when handling such materials great care must be taken to exclude moisture. However if a restricted amount of water is used then oxyalkoxides of definite stoichiometry may be formed. e.g.[76]

$$2Ti(OBu^t)_4 + H_2O \longrightarrow (OBu^t)_3Ti\text{-}O\text{-}Ti(OBu^t)_3 + 2Bu^tOH$$

This limited hydrolysis of alkoxides has been exploited to make materials that are catalytically active. An example of this is the partial hydrolysis of zinc-aluminium alkoxides[77-79]:

$$(RO)_2Al(OR)_2Zn(OR)_2Al(OR)_2 + 2H_2O \longrightarrow (RO)_2Al\text{-}O\text{-}Zn\text{-}O\text{-}Al(OR)_2 + 4ROH$$

The μ-oxoalkoxide so formed is active for the ring opening polymerisation of lactones.

(b) Alcohol Exchange Reactions

Exchange of the alkoxy group of an alkoxide for a different alkoxy group is useful in the preparation of metal alkoxides and as such has been discussed in the section above.

(c) Reaction with Organic Acids

As can be expected from the relative acidities, organic acids react with metal alkoxides to form metal carboxylates. Indeed aluminium tri-carboxylates may be formed as long as all traces of moisture are removed. e.g.[80]

$$Al(OPr^i)_3 + 3CH_3CO_2H \longrightarrow Al(O_2CCH_3)_3 + 3Pr^iOH$$

(d) Meerwein-Ponndorf-Verley Reaction

The reduction of ketones by alcohols is catalysed by metal alkoxides of which aluminium alkoxides are the best. The reaction can be driven to completion by the removal of the volatile ketone formed (often acetone):

$$Me_2HC\text{-}OH + R'_2C{=}O \longrightarrow Me_2C{=}O + R'_2HC\text{-}OH$$

(e) Thermal Decomposition of Alkoxides

Metal alkoxides decompose on heating to the metal oxides, hydroxides or to the metal itself with the evolution of organic species. The mode of decomposition depends not only on the alkoxide but on the conditions of the pyrolysis. For example it is reported that copper(II) methoxide decomposes in air to form copper(II) oxide[67] whereas in the course of the present study, decomposition under vacuum led to the formation of copper metal.

(f) Other Reactions

There are many more reactions of alkoxides: some react with hydrogen halides to form metal halides or mixed alkoxy-halides; some react with esters to form new alkoxides (see transesterification above); some react with glycols to form glycolates which are often less moisture sensitive than alkoxides; some react with thiols to form thiolates.

3.2.4 Uses of Alkoxides

Despite the fact that alkoxides are moisture-sensitive and thus require special handling techniques they have many industrial applications. A brief summary of some of these is given below:

(a) Catalysts

The use of alkoxides as catalysts has already been alluded to in the above discussion in their role as catalysts in the Meerwein-Ponndorf-Verley reaction and in ring opening polymerisations. However there are other systems catalysed by alkoxides: Ziegler-Natta polymerisations[81]; transesterifications[82,83] and polyester formation[84-86].

(b) Polymer Cross-Linking Agents

The ability of certain alkoxides to promote cross-linking makes them useful in a variety of ways, for example titanium and zirconium alkoxides may be used in films where rapid drying is required[87] whilst aluminium, titanium and zirconium alkoxides may be used in conjunction with silicones in the waterproofing of leather where it is believed that the alkoxides promote the curing of the silicone[88].

(c) As Precursors to Metal Oxides, Glasses and Ceramics

One of the major difficulties encountered when dealing with metal alkoxides is their susceptibility to hydrolysis. However it is this very property that has led to a major use of alkoxides: the formation of high purity metal oxides by the pyrolysis of the hydroxides formed on the controlled hydrolysis of alkoxides[89]. The metal alkoxides are readily purified by distillation under reduced pressure or by recrystallisation so the oxides produced are free from impurity.

Glasses which can be formed at low temperatures (800°C) have been made from the products of the cohydrolysis of mixtures of silicon alkoxides and other metal alkoxides[90,91]. These offer scope for the production of high-purity specialised glass films.

Similar, and perhaps more important is the preparation of superconductors via the pyrolysis of hydroxides formed on the hydrolysis of, for example, solutions of barium, yttrium and copper alkoxides[92,93]. Again it is the high purity of the alkoxide precursors which is important in this application.

Therefore it can be seen that alkoxides are useful industrial chemicals, and will certainly become more so if the final application described above can be exploited.

3.3 Carboxylates and Hydroxycarboxylates

Metal carboxylates or metallic soaps as they are sometimes called are, as the names suggest, metal derivatives of carboxylic acids and as such have been known for many years. Metal hydroxycarboxylates are related compounds in which the organic chain of the acid contains one or more hydroxy groups.

3.3.1 Preparation of Carboxylates[94,95]

A review of the large number of synthetic routes to metal carboxylates is given below. The routes, which can be conveniently divided into those employing aqueous reactions and those carried out in non-aqueous systems, are generally more straightforward than those employed in the synthesis of alkoxides.

(a) Aqueous Reactions

Metal carboxylates may be prepared by the reaction at controlled pH of a carboxylic acid or its alkali metal or ammonium salt with metal salts such as chloride, nitrate, sulphate, oxide, hydroxide and carbonate. e.g.

$$MX_n + nRCO_2Y \longrightarrow M(O_2CR)_n + nXY$$

$X = Cl, NO_3, OH,$

$Y = H, Na, K, NH_4$

This is the most straightforward method of preparing metal carboxylates and may be used to prepare copper and zinc carboxylates. e.g.[96]

$$CuCO_3 + 2C_2H_5CO_2H \longrightarrow Cu(O_2CC_2H_5)_2.H_2O + CO_2$$

The hydrated metal carboxylates may be dehydrated by heating to approximately 110°C under vacuum[96,97], but this can also lead to some decomposition occurring for example with the trifluoroacetates of copper and zinc[98].

The methods described above are not suitable for the preparation of aluminium tricarboxylates as they are susceptible to hydrolysis; instead dicarboxylates (i.e. $Al(OH)(O_2CR)_2$) are produced[99,100].

(b) Reactions in Non-aqueous Media

If anhydrous metal carboxylates are required then it is often useful to carry out the preparations in non-aqueous media. Indeed for some metal carboxylates such reactions provide the only suitable synthetic pathway (e.g. $Al(O_2CCH_3)_3$[80]). The preparations involve the reaction of carboxylic acids with metal derivatives in organic solvents.

(i) <u>Reaction with Metal Halides</u>: Aluminium triacetate may be prepared by the reaction of anhydrous aluminium chloride and a mixture of glacial acetic acid and acetic anhydride, the anhydride being used to eliminate any water that may be present[101]:

$$AlCl_3 \quad + \quad 3CH_3CO_2H \longrightarrow Al(O_2CCH_3)_3 \quad + \quad 3HCl$$

This method may also be used to prepare anhydrous copper and zinc carboxylates[98].

(ii) <u>Reaction with Metal Alkoxides</u>: The reaction between aluminium alkoxides and carboxylic acids was alluded to in section 3.2.3. It provides a convenient synthesis of aluminium tricarboxylates with a less reactive side product than in the above reaction (alcohol instead of hydogen chloride). e.g.[80]

$$Al(OPr^i)_3 \quad + \quad 3C_3H_7CO_2H \longrightarrow Al(O_2CC_3H_7)_3 \quad + \quad 3Pr^iOH$$

(iii) <u>Reaction with Other Metal Derivatives</u>: Some metal carboxylates have been prepared using metal alkyls, metal carbonyls and metal hydrides. For example triphenyl aluminium reacts with acetic acid in a stepwise manner to produce aluminium triacetate. The intermediate compounds may be isolated[102]:

$$Ph_3Al + CH_3CO_2H \longrightarrow Ph_2Al(O_2CCH_3) + PhH$$

$$Ph_2Al(O_2CCH_3) + CH_3CO_2H \longrightarrow PhAl(O_2CCH_3)_2 + PhH$$

$$PhAl(O_2CCH_3)_2 + CH_3CO_2H \longrightarrow Al(O_2CCH_3)_3 + PhH$$

Exchange reactions between lower metal carboxylates and higher carboxylic acids have been employed in the preparation of some metal carboxylates. An example is the replacement of acetate by succinate (1,4-butanedioate) in tin(IV) acetate which can be pushed to completion if the acetic acid produced is removed as its toluene azeotrope:[103]

$$Sn(O_2CCH_3)_4 + 2HO_2CCH_2CH_2CO_2H \longrightarrow Sn(O_2CCH_2CH_2CO_2)_2 + 4CH_3CO_2H$$

Copper(II) carboxylates have also been prepared by the anodic dissolution of copper in the relevant carboxylic acid[104].

3.3.2 Preparation of Hydroxycarboxylates

Metal hydroxycarboxylates may be prepared in similar ways to metal carboxylates, with the reaction of the acid with metal salts at controlled pH being used extensively. e.g. Copper(II) lactate[105]

$$2CH_3CH(OH)CO_2H + CuCO_3 \longrightarrow Cu(O_2CCH(OH)CH_3)_2 + CO_2 + H_2O$$

3.3.3 Structural Properties of Carboxylates[94,95,106,107]

Carboxylate ligands may coordinate to metals in a variety of ways. The use of single crystal x-ray diffraction has enabled numerous structures to be unambiguously determined. These may be grouped according to the type of coordination of the carboxylate group.

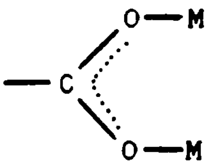
(a) <u>Ionic</u>: Sodium formate is an example of an ionic carboxylate. The electrons in the carboxylate group are delocalised with the two C-O bonds being identical in length (1.27Å)[108].

(b) <u>Unidentate</u>: In this case the metal coordinates to only one of the two available oxygen atoms. An example is lithium acetate dihydrate in which the two C-O bonds are of very different lengths: that in the C-O-M unit is 1.33Å whilst the free carbonyl bond is 1.22Å[109].

(c) <u>Bidentate</u>: The number of compounds in which a carboxylate acts as a bidentate ligand to a metal is limited due to the fact that it necessitates the formation of a four membered ring. However some such compounds are known, for example, zinc acetate dihydrate in which the two Zn-O bonds are very similar in length (2.18, 2.17Å) and one C-O bond is slightly longer than the other (1.30, 1.38Å)[110].

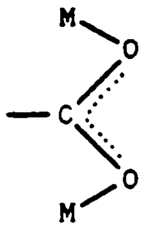
(d) <u>Bridging</u>: Carboxylate groups readily bridge between metals. In most cases a M-O-C-O-M bridge is formed which is different to the M-O-M systems observed in alkoxide chemistry. There are several possible modes of bridging:

(i) Syn-Syn



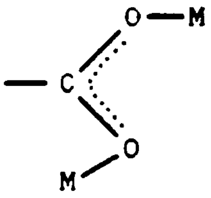
This is the most commonly obsereved mode and an example is copper(II) acetate dihydrate[111].

(ii) Anti-Anti



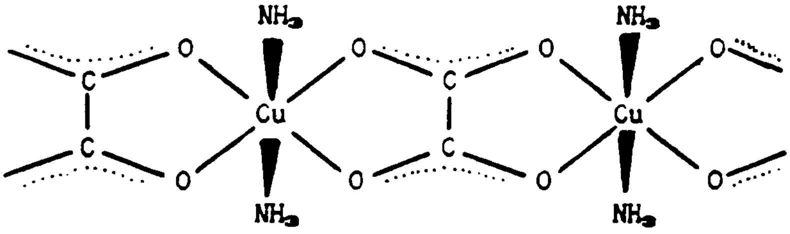
This mode is usually observed in polymeric metal carboxylates for example copper(II) formate tetrahydrate[112]. The formation of a polymeric system is favoured by the smaller size of the formate ion.

(iii) Anti-Syn



An example of this mode of bridging which is also usually observed in polymeric systems is anhydrous copper(II) formate[113].

The coordination modes described for carboxylates are also equally valid for dicarboxylates (derivatives of dibasic acids, e.g. oxalic). However the presence of two carboxylate groups per ligand increases the scope for bridging. Tetradentate bridging is the most common type and is observed in, for example, diamminecopper(II) oxalate dihydrate[114]:



3.3.4 Structural Properties of Hydroxycarboxylates[115]

The coordination of the carboxylate group to metals in hydroxycarboxylates may occur in the ways described above. However a more interesting aspect of the structural chemistry of metal hydroxycarboxylates is whether the oxygen of the hydroxy group coordinates to the metal. Generally in 2-hydroxyalkanoates the oxygen does coordinate to the metal, forming a stable five membered ring (e.g. in copper(II) lactate hemihydrate[105] and zinc lactate dihydrate[116]) whilst in 2-hydroxybenzoates such coordination does not occur (e.g. copper(II) 2-hydroxybenzoate tetrahydrate[117] and zinc 2-hydroxybenzoate dihydrate[118] - see Figure 7.2, page 122). This difference is presumably due to the greater flexibility of the aliphatic system compared to the aromatic system as well as the reduced availability of the oxygen electron pairs due to resonance with the aromatic group.

3.3.5 Reactions of Carboxylates and Hydroxycarboxylates

In comparison to the very reactive metal alkoxides, metal carboxylates and hydroxycarboxylates have a more limited chemistry. It is their thermal chemistry which has received most study and the following section summarises this.

The thermal decarboxylation of some metal carboxylates has been used in the synthesis of organometallic compounds of, for example, mercury, tin and lead[119] whilst the thermal decomposition of others gives ketones, thus calcium acetate produces acetone:[120]

$$Ca(O_2CCH_3)_2 \xrightarrow{\Delta} CaCO_3 + (CH_3)_2C{=}O$$

A review of the thermal decompositions of various metal carboxylates (e.g. Al, Fe, Co, Ni, Cu and Zn; formates, acetates and oxalates) showed that metals or metal oxides were produced[121]. More detailed studies have been made on some systems including formates, oxalates and 2-hydroxybenzoates.

(a) Formates

The thermal decomposition of copper(II) formate has been studied under various conditions:

(i) Air: The residue obtained on heating copper(II) formate to 200°C in air was a mixture of copper(II) oxide and copper(I) oxide[122,123].

(ii) Vacuum: In a similar experiment carried out under reduced pressure the residue did not contain any copper(II) oxide but consisted of predominantly copper metal with only a minor amount of copper(I) oxide[122,123]. It was also shown that this copper could be deposited on to various ceramics, glasses or metals[124].

(iii) Inert Atmosphere: A metallic residue was obtained when the decomposition was carried out in a stream of an inert gas (nitrogen or argon)[125].

(iv) Self-Generated Atmosphere: When copper(II) formate was heated in a sealed ampule, carbon dioxide and hydrogen were evolved and metallic copper remained:[126]

$$Cu(O_2CH)_2 \xrightarrow{\Delta} Cu + 2CO_2 + H_2$$

(v) Other Atmospheres: When an atmosphere of ammonia was used then the decomposition temperature was significantly lowered (to 140°C). This was due to the formation of a tetrammine complex but the residue was still metallic copper[127]. A similar effect was observed on the decomposition to copper metal of monoethanolamine complexes of copper(II) formate, with temperatures of 150°C being used[128].

The thermal decomposition of zinc formate was found to produce zinc oxide regardless of the conditions employed[123].

(b) Oxalates

Copper(II) oxalate decomposes in an inert atmosphere or under vacuum at 300°C to give predominantly copper metal with trace amounts of oxide being present:[129]

$$Cu(C_2O_4) \xrightarrow{\Delta} Cu + 2CO_2$$

The same decomposition but in air led to the formation of copper(II) oxide[130].

Zinc oxalate decomposes at 300°C in air or under vacuum to give zinc oxide:[121,129]

$$Zn(C_2O_4) \xrightarrow{\Delta} ZnO + CO + CO_2$$

(c) 2-Hydroxybenzoates

The hydrated 2-hydroxybenzoates of manganese, nickel and zinc all decompose in three stages to their oxides at temperatures of about 350°C in air and 500°C in nitrogen[131]. The first stage was dehydration which was followed by the successive loss of the acid groups.

3.3.6 Uses of Carboxylates and Hydroxycarboxylates[94,115,130]

Metal carboxylates and hydroxycarboxylates are important industrial chemicals and as such have a large number of applications. A detailed review of these is beyond the scope of this thesis and therefore some illustrative examples of their uses are given below.

(a) Carboxylates

(i) Soaps The sodium or potassium salts of long chain carboxylic acids are used as soaps.

(ii) Catalysts Metal carboxylates are of use as catalysts, for example copper(I) carboxylates may be used in homogeneous hydrogenations[132].

(iii) Building Materials Metal carboxylates may be used to waterproof concrete and also to plasticise mortar: a small amount (<0.1%) of sodium carboxylates added to mortars greatly increases plasticity and also enables the proportion of cement present to be lowered[133] whilst concretes made with some zinc oleate (9-octadeceneoate) present are waterproof[134].

(iv) Fuel Additives The efficiency of certain fuels is enhanced on the addition of some metal carboxylates for example copper(II) naphtheneates (alkylcyclopentane carboxylic acids) help to prevent deposits in furnaces fired by coal or heavy oil[135].

(v) Other Uses Copper and zinc naphtheneates are fungicidal and may be used to preserve textiles and wood[136]; zinc stearate (octadecanoate) may be used to increase the covering ability of films and paints[137]; many cosmetic products contain metal carboxylates, for example zinc stearate is often found in face powders as it improves spreading and adherence properties[138].

(b) Hydroxycarboxylates

Metal hydroxycarboxylates have a wide variety of uses, many of which involve the chelation of metals, for example complexes of copper(II) tartrate are used as Fehling's solution in organic chemistry; metal complexes (e.g. calcium and sodium) of 2-hydroxybenzoic acid are used as antipyretics and in the treatment of rheumatism and some hydroxycarboxylates (e.g. citrates) have been found to improve surface quality in electroplating baths[139].

CHAPTER 4

Precipitation Reactions of Copper and Zinc Oxalates, Formates and Adipates

4.1 Introduction

This chapter describes attempts to prepare mixed metal compounds of copper and zinc by co-precipitation and co-crystallisation reactions as they provided, in theory, simple ways of incorporating copper and zinc into single compounds. Indeed there is evidence that such reactions do lead to the formation of mixed metal salts[140,141], but the work described below indicates that the reactions may not be as straightforward as reported. A discussion of the work carried out on oxalates, formates and adipates is followed by the experimental details.

4.2 Discussion

Co-precipitation or co-crystallisation reactions of two metal salts to form a mixed metal species requires the formation of a lattice in which there are coordination sites of a suitable size and geometry for each of the metals concerned. This does not necessarily mean that the metals have to be of the same size and geometry as some structures provide sites of varying size and geometry. An example of this is the spinels (e.g. $ZnAl_2O_4$) where there are tetrahedral as well as octahedral metal sites. However if the mixed metal species involves the exchange of one metal in the lattice for another then the metals do need to be of similar size and coordination geometry. Unfortunately for copper and zinc the latter is not the case.

Zn^{2+} has a d^{10} electronic configuration and thus its stereochemistry is determined solely by considerations of size, electrostatic forces and covalent bonding forces as there is no crystal field stabilisation effect. It is commonly observed with coordination numbers of 4, 5 or 6 with associated regular geometries: tetrahedral or planar when 4 coordinate; trigonal bipyramidal or square pyramidal when 5 coordinate; octahedral when 6 coordinate.

Cu^{2+} has a d^9 electronic configuration and is thus subject to Jahn-Teller distortion if it is placed in an environment of cubic symmetry. That is to say that with a coordination number of 4 a distorted tetrahedral geometry is normally observed and with a coordination number of 6 a distorted octahedral geometry is normally observed.

It is therefore unlikely that Zn^{2+} and Cu^{2+} can interchange in crystal lattices despite having similar ionic radii (Cu^{2+}, 0.6-0.9Å; Zn^{2+}, 0.74Å)[142]. It is more likely that Cu^{+} and Zn^{2+} can interchange as in this case both the copper and zinc have a d^{10} electron configuration and thus their geometries should match, but an extra cation would be required to balance the charges and the structure would have to be able to accomodate the different sized cations (Cu^{+}, 0.96Å; Zn^{2+}, 0.74Å)[142]. Nevertheless one such compound, $(N(CH_3)_4)Cu^{I}Zn^{II}(CN)_4$, has recently been observed[143].

4.2.1 Oxalates

Metal oxalates are potentially very good precursors from which to prepare catalysts by thermal decomposition as they decompose cleanly to metals and metal oxides with no organic contamination[121], liberating carbon dioxide and carbon monoxide. Furthermore an anomalous thermal decomposition of a co-precipitated copper-zinc oxalate has been observed[140]: the thermal decomposition, as followed by thermo-gravimetry, proceded in two stages, firstly dehydration at 100-120°C followed by decomposition at 290-350°C. This contrasts with the thermal decomposition of a physical mixture of copper oxalate and zinc oxalate which decomposed in three stages, firstly dehydration at 100-120°C followed by two separate decomposition stages at 280-310°C and 380-400°C. The explanation given for this was that an interpenetrating matrix of copper and zinc oxalates i.e. a solid solution had been formed.

(a) Simple Metal Oxalates

Copper(II) oxalate and zinc oxalate were prepared by the reaction of the metal sulphates with oxalic acid in aqueous solution:

$$2CuSO_4.5H_2O + 2C_2O_4H_2 \longrightarrow 2Cu(C_2O_4).\frac{1}{2}H_2O + 2H_2SO_4 + 9H_2O$$

These preparations whilst relatively straightforward, illustrated some properties of the metal oxalates which were to prove important throughout the subsequent work. The solubilities of the oxalates are exceedingly low in water (copper(II) oxalate hemihydrate, 0.00253g/100ml; zinc oxalate dihydrate, 0.00079g/100ml)[144] and the precipitates produced were very fine despite adopting normal techniques to increase crystallite size (slow addition of reagents, boiling to aggregate). This made filtrations difficult and precluded the washing of products. The infra red spectra of the two oxalates were very similar, both consisting of a few strong, broad, absorptions (e.g. at 3660-3040, 1680, 1320 and 820cm^{-1}). The varying degrees of hydration observed gave difficulties when dealing with elemental analyses and for this reason all the precipitated samples were exposed to air, preferably overnight, so as to equilibrate the waters of crystallisation present.

(b) Co-Precipitation Reactions

Several co-precipitation reactions were carried out using different sources of the oxalate anion, varying the proportions of the reagents and using different methods of reaction. These experiments showed that mixed-metal salts were not being formed, a conclusion later confirmed by x-ray powder photography. The infra red spectra recorded were of limited use as they were all very similar to the spectra of the individual compounds.

The products of reactions of an equimolar solution of copper(II) sulphate and zinc sulphate with solutions of equivalent quantities of potassium oxalate, oxalic acid or ammonium oxalate added rapidly with vigorous stirring all contained copper and zinc in approximately 1:1 ratios:

$$Cu^{2+} + Zn^{2+} + 2(C_2O_4)^{2-} \longrightarrow \text{"}CuZn(C_2O_4)_2.xH_2O\text{"}$$

The use of potassium oxalate led to the incorporation of potassium in the final product. A portion of the product made using ammonium oxalate was thermally decomposed under a static vacuum. Heating to 350°C for 2 hours led to the evolution of a small quantity of carbon monoxide and a larger quantity (c.a. 3 molar proportions) of carbon dioxide. The residue consisted primarily of copper, zinc and oxygen with a small amount of organic contamination showing that decomposition was not quite complete. The ratio of carbon dioxide to carbon monoxide evolved indicated that half of the metal in the residue would have to be metallic:

$$\text{"CuZn(C}_2\text{O}_4\text{)}_2\text{"} \xrightarrow{\Delta} \text{ZnO} + \text{Cu} + 3\text{CO}_2 + \text{CO}$$

The effect of altering the order of addition so that the solution of the metal sulphates was added to a solution of ammonium oxalate was investigated. The rate of addition did not affect the product, which contained copper and zinc in the ratio 1:1. The product was shown to consist of a mixture of the individual metal oxalates by x-ray powder photography: the lines observed for the co-precipitated product matched those of a physical mixture of copper(II) oxalate hemihydrate and zinc oxalate dihydrate.

Two reactions were then carried out where half an equivalent of ammonium oxalate was added to a stirred solution containing equimolar amounts of copper(II) sulphate and zinc sulphate:

$$\text{Cu}^{2+} + \text{Zn}^{2+} + (\text{C}_2\text{O}_4)^{2-} \longrightarrow$$

In one case a rapid addition was used which led to the precipitation of a product with a copper to zinc ratio of 14:1, whilst in the other case a dropwise addition was used which led to the precipitation of a product with a copper to zinc ratio of 38:1. Thus it was apparent that copper(II) oxalate was being precipitated preferentially to zinc oxalate and that it was unlikely that mixed salts were being formed in any of the above reactions. It is interesting that the copper salt precipitates rather than the less soluble zinc salt. A possible explanation for this is that the solubilities of the two oxalates, quoted above, were measured in neutral solution whereas in this situation the solution will be acidic which may well alter the solubilities.

A possible reason why the above reactions were not producing mixed salts may have been the very low solubility of the metal oxalates causing them to precipitate preferentially to any mixed salt. Thus the more soluble ammine complexes were prepared and a co-crystallisation reaction was attempted.

Diamminecopper(II) oxalate dihydrate was prepared by dissolving copper(II) oxalate in dilute ammonia and allowing the blue crystals to form[114]:

$$Cu(C_2O_4) \quad + \quad 2NH_4OH \longrightarrow Cu(C_2O_4)(NH_3)_2.2H_2O$$

The zinc analogue was made in a similar fashion. Both of these products were dried in air as the ammine was partially removed if they were dried in vacuo.

The addition of a solution containing equimolar amounts of copper(II) and zinc oxalates to an aqueous solution of ammonia resulted in a series of compounds being collected. The ratio of copper to zinc varied considerably in these compounds which were shown (by x-ray diffraction, as above) to consist of mixtures of the individual complexes.

(c) <u>Use of Oxalato Complexes</u>

The use of oxalato complexes as potential sources of mixed metal compounds was investigated once it became apparent that co-precipitation reactions were resulting in physical mixtures of oxalates rather than mixed metal species.

Potassium tris-oxalato aluminate was readily prepared by dissolving aluminium shavings in hot potassium hydroxide solution and adding a solution of oxalic acid with the addition of ethanol inducing crystallisation[145]. Overall:

$$6KOH \quad + \; 2Al \quad + \quad 6C_2O_4H_2 \longrightarrow 2K_3Al(C_2O_4)_3.3H_2O \quad + \quad 3H_2$$

An attempt to prepare the copper salt of the tris-oxalato aluminate by the addition of a solution of copper(II) chloride to a solution of the potassium salt of the complex led to the precipitation of copper(II) oxalate. This happened as, in aqueous solution, the tris-oxalato aluminate anion is in equilibrium with, ultimately, aluminium cations and oxalate anions:

$$Al(C_2O_4)_3^{3-} \rightleftharpoons Al(C_2O_4)_2^{-} + (C_2O_4)^{2-}$$

$$Al(C_2O_4)_2^{-} \rightleftharpoons Al(C_2O_4)^{+} + (C_2O_4)^{2-}$$

$$Al(C_2O_4)^{+} \rightleftharpoons Al^{3+} + (C_2O_4)^{2-}$$

The equilibria normally lie well to the left so the concentration of oxalate anion would be very small. However on the introduction of some copper(II) cations, copper(II) oxalate would be precipitated, due to its very low solubility, thus removing the oxalate anion from solution. This has the effect of displacing the equilibria to the right and this will continue until either all the copper(II) cations or oxalate anions have been removed from the solution.

Ammonium bis-oxalato cuprate(II) was prepared by dissolving copper(II) oxalate in a warm solution of ammonium oxalate, blue crystals separating on cooling[146]:

$$(NH_4)_2(C_2O_4).2H_2O + Cu(C_2O_4) \longrightarrow (NH_4)_2Cu(C_2O_4)_2.2H_2O$$

The reaction of this with zinc sulphate led to the precipitation of zinc oxalate for reasons similar to those described above. Therefore it appears that oxalato complexes are unsuitable compounds to use in the preparation of mixed metal species.

4.2.2 Formates

The preparations of copper(II) formate and zinc formate are discussed in the next chapter (see section 5.2.2). Co-crystallisation reactions of solutions of copper(II) formate and zinc formate were carried out due to the contention that crystalline mixed metal salts would result[141]. The experiments, carried out by a final year undergraduate student as a research project, showed that such materials could be made[147]. However they made up only a small proportion of the mixture of crystals that were produced with the remainder being single metal salts. Also the amount of copper and zinc present in them varied considerably and they had to be separated using a microscope and tweezers. For these reasons it was not considered to be a practical proposition to use them as precursors for catalysts.

4.2.3 Adipates

Copper(II) adipate and zinc adipate were readily prepared by reaction of the metal nitrate with ammonium adipate at 70°C[148,149]. e.g.

$$Cu(NO_3)_2 + (NH_4)_2(O_2C(CH_2)_4CO_2) \longrightarrow Cu(O_2C(CH_2)_4CO_2) + 2NH_4NO_3$$

A crystal structure of adipato (N,N'-diethylethylenediamine) copper(II) shows it to consist of dimeric units containing 18 member rings[150]. It was assumed that, due to the length and thus flexibility of the organic chain, some differences in coordination environments of the two metals might be tolerated and thus that a mixed salt might result from a co-precipitation reaction. However the result of adding a solution of equimolar proportions of copper(II) nitrate and zinc nitrate to a solution of ammonium adipate was the formation of a precipitate which was observed, using a microscope, to consist of green particles and white particles i.e. a physical mixture of copper(II) adipate and zinc adipate.

4.3 Experimental

4.3.1 Oxalates

(a) Preparation of Copper(II) Oxalate Hemihydrate

To a solution of oxalic acid dihydrate (4.00g, 0.032mol) in water (100ml) was added slowly, with vigorous stirring, a solution of copper(II) sulphate pentahydrate (5.00g, 0.020mol) in water (100ml) affording a very fine blue precipitate. The mixture was warmed in an attempt to increase the crystallite size, cooled, filtered (the filtrate was cloudy and blocked fine (No. 4) sinters), the blue solid dried in vacuo and then exposed to air overnight so as to equilibrate the waters of crystallisation. Yield 0.75g (23%). The product was characterised as follows:

Analysis Found: C,15.2; H,0.5; Cu,38.6 %.

$C_2HCuO_{4.5}$ Requires: C,15.0; H,0.5; Cu,39.6 % (hemihydrate)

$C_2H_2CuO_5$ Requires: C,14.2; H,1.2; Cu,37.5 % (monohydrate)

Infra Red (nujol, cm^{-1}): 3640-3080(br); 3000-2800(nujol); 1680(s); 1460, 1380(nujol); 1360; 1320; 825; 510; 390.

(b) Preparation of Zinc Oxalate Dihydrate

To a solution of oxalic acid dihydrate (4.00g, 0.032mol) in water (100ml) was added slowly, with vigorous stirring a solution of zinc sulphate heptahydrate (5.76g, 0.02mol) in water (100ml) affording a fine white precipitate. The mixture was filtered (the filtrate was again cloudy) and the white solid washed with water, dried in vacuo and exposed to air overnight (as above). Yield 2.73g (72%). The product was characterised as follows:

<u>Analysis</u> Found: C,12.5; H,2.1; Zn,34.6 %

$C_2H_4O_6Zn$ requires: C,12.7; H,2.1; Zn,34.5 %

<u>Infra Red</u> (nujol, cm^{-1}): 3700-3040(br); 3000-2800(nujol); 1640(s)

1460, 1370(nujol); 1320, 820, 500, 460.

(c) <u>Reactions of Copper and Zinc Sulphates with Oxalates</u>

A series of reactions were carried out with the general stoichiometry:

$$xCu^{2+} + xZn^{2+} + yox^{2-} \longrightarrow$$

Details of these reactions are given below:

(i) To a solution of copper(II) sulphate pentahydrate (5.00g, 0.02mol) and zinc sulphate heptahydrate (5.76g, 0.02mol) in water (100ml) was added rapidly, with vigorous stirring, an aqueous solution of potassium oxalate monohydrate (7.38g, 0.04mol, 100ml) affording a pale blue precipitate. The mixture was filtered (the filtrate was again cloudy) and the pale blue solid was dried in vacuo and exposed to air overnight (as above). Yield 3.77g (55% if $CuZnox_2.2H_2O$). The product was characterised as follows:

<u>Analysis</u> Found: C,12.6; H,1.3; Cu,17.0; Zn,15.0; K,4.0 %

$C_4H_4CuO_{10}Zn$ Req: C,14.1; H,1.2; Cu,18.6; Zn,19.2 %

<u>Infra Red</u> (nujol, cm^{-1}): 3660-3040(br); 3000-2800(nujol); 1660(s);

1460, 1380(nujol); 1320, 825 500.

(ii) The above reaction was repeated, but using oxalic acid dihydrate (5.04g, 0.04mol) rather than the potassium salt. Yield of the fine blue solid was 1.70g (25% if $CuZnox_2.2H_2O$ - filtrate again cloudy). The product was characterised as follows:

Analysis	Found:	C,13.2; H,1.2; Cu,18.1; Zn,18.0 %
	$C_4H_4CuO_{10}Zn$ Req:	C,14.1; H,1.2; Cu,18.6; Zn,19.2 %
Infra Red	As above.	

(iii) The above reaction was repeated but this time using ammonium oxalate monohydrate (5.68g, 0.04mol). Yield of the fine blue solid was 4.51g (66% if $CuZnox_2.2H_2O$ - filtrate again cloudy). The product was characterised as follows:

Analysis	Found:	C,12.9; H,1.6; Cu,16.7; Zn,17.7; N,0.7 %
	$C_4H_4CuO_{10}Zn$ Req:	C,14.1; H,1.2; Cu,18.6; Zn,19.2 %
Infra Red	As above.	

(iv) The above reaction was repeated but this time using half the amount of ammonium oxalate monohydrate (2.84g, 0.02mol). Yield of the fine blue solid was 1.63g (48% if $CuZnox_2.2H_2O$ - filtrate again cloudy). The product was characterised as follows:

Analysis	Found:	C,14.5; H,0.7; Cu,33.1; Zn,2.5; N,0.0 %
	$C_4H_4CuO_{10}Zn$ Req:	C,14.1; H,1.2; Cu,18.6; Zn,19.2 %
Infra Red	As above.	

(v) The above reaction was repeated but this time the ammonium oxalate was added dropwise. Yield of the fine blue solid was 0.79g (23% if $CuZnox_2.2H_2O$ - filtrate again cloudy). The product was characterised as follows:

Analysis Found: C,14.4; H,0.6; Cu,36.6; Zn,1.00; N,0.0 %

$C_4H_4CuO_{10}Zn$ Req: C,14.1; H,1.2; Cu,18.6; Zn,19.2 %

Infra Red As above.

(vi) To a solution of oxalic acid dihydrate (6.00g, 0.048mol) in water (100ml) was added, rapidly, with vigorous stirring, a solution of copper(II) sulphate pentahydrate (5.00g, 0.02mol) and zinc sulphate heptahydrate (5.76g, 0.02mol) in water (100ml). The resulting blue precipitate was separated and dried as above. Yield 4.09g (60% if $CuZnox_2.2H_2O$ - filtrate again cloudy). The product was characterised as follows:

Analysis Found: C,13.4; H,1.5; Cu,18.1; Zn,18.7 %

$C_4H_4CuO_{10}Zn$ Req: C,14.1; H,1.2; Cu,18.6; Zn,19.2 %

Infra Red As above.

(vii) The above reaction was repeated but this time the solution of metal sulphates was added dropwise. Yield of the fine blue solid was 5.60g (82% if $CuZnox_2.2H_2O$ - filtrate again cloudy). The product was characterised as follows:

Analysis Found: C,13.1; H,1.4; Cu,18.1; Zn,18.2 %

$C_4H_4CuO_{10}Zn$ Req: C,14.1; H,1.2; Cu,18.6; Zn,19.2 %

Infra Red As above.

X-ray powder photographs were taken of copper(II) oxalate hemihydrate, zinc oxalate dihydrate, a physical mixture of these and of the product from "(vii)" above. The d values were calculated and are tabulated below (in ångströms):

Cuox.½H_2O	Znox.2H_2O	Physical Mixture	Co-precipitated
	2.31	2.31	2.32
1.92	1.95	1.92	1.92
	1.49	1.49	1.50
1.34	1.30	1.31	1.31
1.28		1.28	1.28
1.20		1.20	1.21
	1.16	1.16	1.16
1.12		1.13	1.13
	1.10	1.10	1.10
1.04	1.02	1.02	1.03
	1.01	1.01	1.02
0.96	0.97	0.96	0.96
	0.89	0.89	0.89

(d) Bisammine complexes of Copper and Zinc Oxalates

(i) A portion of copper(II) oxalate hemihydrate was dissolved in aqueous ammonia (2M), and the resulting dark blue solution left overnight to crystallise. Blue crystals were formed which were filtered off and allowed to dry in air. These were characterised as follows:

Analysis Found: C,10.6; H,4.0; Cu,28.8; N,11.6 %

$C_2H_{10}CuN_2O_6$ Req: C,10.8; H,4.6; Cu,28.7; N,12.6 %

(dihydrate)

Infra Red (nujol, cm^{-1}): 3660-3000(b); 3460(sh); 3340(sh); 3280(sh) 3000-2800(nujol); 1640(s); 1460, 1380(nujol); 1365(sh) 1310; 1280; 800; 745; 535; 500.

(ii) A portion of zinc oxalate dihydrate was dissolved in aqueous ammonia (2<u>M</u>), and the resulting clear solution left overnight to crystallise. White crystals were formed which were filtered off and allowed to dry in air. These were characterised as follows:

<u>Analysis</u> Found: C,10.4; H,4.2; Zn,30.0; N,10.8 %

$C_2H_{10}N_2O_6Zn$ Req: C,10.8; H,4.5; Zn,29.3; N,12.5 %

(dihydrate)

<u>Infra Red</u> (nujol, cm^{-1}): 3640-3000(br); 3430(sh); 3340(sh); 3280(sh); 3180(sh); 3000-2800(nujol); 1680(s); 1640; 1595; 1460, 1380(nujol); 1320; 1260; 800.

(iii) To an aqueous solution of ammonia (100ml, 2<u>M</u>) was added copper(II) oxalate hemihydrate (4.00g, 0.025mol) and zinc oxalate dihydrate (4.72g, 0.025mol) forming a clear, dark blue, solution which was left to crystallise. A series of precipitates were collected (5 in all) of varying colour: blue/green, pale blue and dark blue. Two of these were characterised:

<u>Analysis</u> Found: Ppt 1 C,10.3; H,3.6; Cu, 4.1; Zn,25.2; N, 8.0 %

Ppt 2 C, 9.9; H,3.6; Cu,21.1; Zn, 7.8; N,10.7 %

<u>Infra Red</u> (nujol, cm^{-1}): Sum of spectra for individual compounds.

X-ray powder photographs were recorded of the separate complexes as well as for the two mixtures analysed above, (only most intense lines given):

$Cu(ox)(NH_3)_2.2H_2O$	$Zn(ox)(NH_3)_2.2H_2O$	Ppt 1	Ppt 2
	3.13	3.06	
2.97			2.92
2.61		2.61	2.61
	2.17	2.15	
2.11			2.14
	1.83	1.85	1.85
	1.57	1.58	
1.42			1.42
1.39	1.34		
1.38			1.38
1.33			1.33
	1.18	1.17	
	1.15	1.14	

(e) Oxalato complexes of Copper, Zinc and Aluminium

(i) Preparation of Potassium tris-oxalato Aluminate Trihydrate

To a slurry of aluminium shavings (1.00g, 0.037mol) in water (10ml) was added, gradually, an aqueous solution of potassium hydroxide (30ml, 3M). The mixture was boiled until the effervescence had receded and all the aluminium had dissolved. To the clear solution was added water (10ml) followed by oxalic acid dihydrate (approx 14.g, 0.11mol) slowly, until the precipitate just dissolved on boiling. The solution was cooled and ethanol (50ml) was added to induce crystallisation. The white crystals were separated by filtration and dried in air. Yield 11.5g (67%). The product was analysed as follows:

Analysis	Found:	C,15.6; H,0.8; Al,6.5; K,23.4 %
	$C_6H_6AlK_3O_{16}$ Req:	C,15.6; H,1.3; Al,5.8; K,23.4 %

Infra Red (nujol, cm^{-1}): 3700-2500(br); 3000-2800(nujol); 2200-1500(br); 1400; 1270; 910; 805; 580; 440.

(ii) Reaction of Potassium tris-oxalato Aluminate with Copper(II) Chloride

To a solution of potassium tris-oxalato aluminate trihydrate (4.6g, 0.01mol) in water (30ml) was added a solution of copper(II) chloride dihydrate (2.56g, 0.015mol) in water (30ml) forming a pale blue precipitate. The mixture was filtered (the filtrate was cloudy) and the product dried in air. Yield 0.32g. The product was identified as predominantly copper(II) oxalate hemihydrate as follows:

Analysis	Found:	C,14.9; H,1.0; Cu,37.8; K,1.4; Al,Cl,0.0 %
	$C_2HCuO_{4.5}$ Req:	C,15.0; H,0.6; Cu,39.6 %

Infra Red (nujol, cm^{-1}): As for $Cu(C_2O_4).½H_2O$ (see 4.3.1 a)

(iii) Preparation of Ammonium bis-oxalato Cuprate(II) Dihydrate

To an aqueous solution of ammonium oxalate was added copper(II) oxalate hemihydrate and the mixture warmed leading to a clear blue solution. On allowing this to stand blue crystals separated which were characterised as follows:

Analysis	Found:	C,14.8; H,3.6; Cu,18.7; N,8.5 %
	$C_4H_{12}CuN_2O_{10}$ Req:	C,15.4; H,3.9; Cu,20.4; N,9.0 %

Infra Red (nujol, cm^{-1}): 3600-3000(br); 3520(sh); 3400(sh); 3200(sh); 3000-2800(nujol); 1650(br); 1410; 1385(nujol); 900; 810(s); 540; 500.

(iv) Reaction of Ammonium bis-oxalato Cuprate(II) with Zinc Sulphate

The addition of an aqueous solution of zinc sulphate to a solution of ammonium bis-oxalato cuprate(II) led to the precipitation of zinc oxalate dihydrate, contaminated with copper:

Analysis	Found:	C,12.4; H,2.0; Zn,28.3; Cu,5.5; N,0.6 %
	$C_2H_4O_6Zn$ Req:	C,12.7; H,2.1; Zn,34.5 %

Infra Red (nujol, cm^{-1}): As for $Zn(C_2O_4).2H_2O$ (see 4.3.1 b)

(f) Thermal Decomposition of Co-precipitated Copper-Zinc Oxalate

A sample of a co-precipitated copper-zinc oxalate (from 4.3.1, c, (iii), 0.473g) was placed in a horizontal pyrolysis tube and the tube evacuated (for details see Appendix 1). The tube was then heated to 350°C for 2 hours during which time the solid turned a dark red-brown colour. The small quantity of non-condensable volatiles was shown to contain carbon monoxide (ir). The much larger (ca 4 times by volume) quantity of condensable volatiles was shown to contain carbon dioxide and water (ir). A mass loss of 0.266g was observed (theoretical if residue copper metal/zinc oxide, 0.272g). The residue contained a small amount of carbon (2.8%), no hydrogen, copper (38.0%), zinc (41.6%) and oxygen (17.6% by difference) and was assumed to consist of copper metal and zinc oxide with a small amount of residual organic material.

4.3.2 Formates

The preparation and dehydration of copper and zinc formates is discussed in the next chapter (see 5.2.2, 5.3.1 d and 5.3.1 e.). Studies on co-crystallisation reactions carried out by a final year undergraduate student involved allowing solutions containing copper(II) formate and zinc formate in differing concentrations to crystallise[147]. The materials so produced consisted of copper(II) formate tetrahydrate, zinc formate dihydrate and some mixed crystals in which the copper to zinc ratio varied considerably. These were separated manually making use of a microscope. The crystals of mixed composition maintained their appearance in a desiccator unlike those of pure copper(II) formate tetrahydrate which quickly became pale blue on their surface due to the loss of some water of crystallisation.

4.3.3 Adipates

(a) Preparation of Copper(II) Adipate

To a solution of copper(II) nitrate (100ml,0.2M) at 70°C was added a solution of ammonium adipate (100ml,0.2M) and the mixture stirred at 70°C for 30 minutes. Filtration of the hot solution afforded a dark green product which was washed (water), dried in vacuo, and exposed to air overnight to equilibrate water of crystallisation. Yield 2.93g (68%). The product was characterised as follows:

Analysis Found: C,33.1; H,3.9; Cu,29.4 %.
$C_6H_8CuO_4$ Req: C,34.7; H,3.9; Cu,30.6 % (anhydrous).
$C_6H_9CuO_{4.5}$ Req: C,33.3; H,4.2; Cu,29.3 % (hemihydrate)

Infra Red (nujol, cm^{-1}): 3660-3000(br); 3000-2800(nujol); 1580(s); 1460(nujol); 1430(s); 1410(sh); 1380(nujol); 1330(s); 1315;

1270; 1260; 1210; 1155; 1120; 1090; 1070; 930; 880; 870; 765(s); 740; 725; 690; 660; 635; 595; 580; 445; 385.

(b) Preparation of Zinc Adipate

This was prepared in the same way as copper(II) adipate but using zinc nitrate solution (100ml,0.2M). The yield of the white powder was 3.42g (82%) and it was characterised as follows:

Analysis	Found:	C,33.9; H,3.7; Zn,30.2 %.
	$C_6H_8ZnO_4$ Req:	C,34.4; H,3.9; Zn,31.2 % (anhydrous).
	$C_6H_9ZnO_{4.5}$ Req:	C,33.0; H,4.2; Zn,29.9 % (hemihydrate)

Infra Red (nujol, cm^{-1}): 3400(br,w); 3000-2800(nujol); 1590(sh); 1535(s); 1455(nujol); 1410(sh); 1405; 1380(nujol); 1225; 1120; 950; 905; 740; 620; 450.

(c) Co-precipitation of Copper and Zinc Adipates

To an aqueous solution of ammonium adipate (200ml,0.2M) at 70°C was added, dropwise, with vigorous stirring, a solution of copper(II) nitrate trihydrate (4.83g, 0.02mol) and zinc nitrate hexahydrate (5.95g, 0.02mol) in water (200ml). The solution initially turned blue and then turned green as precipitation started (after ca 150ml had been added). The mixture was stirred at 70°C for 30 minutes before filtering the green solid, washing (water) and drying in air. Yield 6.88g (83%). The product was characterised as follows:

Analysis	Found:	C,32.6; H,3.7; Cu,15.2; Zn,16.4 %.
	$C_{12}H_{16}CuO_8Zn$ Req:	C,34.6; H,3.9; Cu,15.2; Zn,15.7 %

Infra Red Sum of spectra for individual compounds.

Examination of the product using a microscope (x60) clearly showed two components: a dark green one and a white one.

CHAPTER 5

Preparation and Thermal Decomposition of Alkoxides and Carboxylates of Aluminium, Copper and Zinc

5.1 Introduction

This chapter describes the preparation and thermal decomposition of various single metal alkoxides and carboxylates of aluminium, copper and zinc. The decompositions described were carried out to act as controls for the mixed decompositions described in chapter 6. A discussion of the preparations and decompositions is followed by the experimental details.

5.2 Discussion

5.2.1 Preparations

The preparative chemistry described in this chapter consists mainly of literature preparations. Nonetheless there are several points arising from the work that are worthy of discussion. The compounds prepared were characterised by elemental analysis and by infra red spectroscopy. In some cases, notably that of zinc methoxide, low carbon analyses were observed due to hydrolysis of the product before or during analysis. The infra red spectra were useful in several of the preparations: in the case of alkoxides they showed that the products had not undergone hydrolysis (on exposure of the mulls to air the alkoxides were very rapidly hydrolysed signified by the appearance of a broad absorption at 3500-3000cm^{-1}) whilst in the case of carboxylate dehydrations the disappearance of the broad absorptions at 3700-2500cm^{-1} showed that all the water had been driven off.

The preparation of aluminium methoxide via the reaction of aluminium iso-propoxide with methanol is an example of a standard reaction type of an alkoxide, alcohol exchange[37]:

$$M(OR)_x + xR'OH \longrightarrow M(OR')_x + xROH$$

The iso-propoxide has a tetrameric structure[63] and is soluble in iso-propanol whereas the methoxide produced with its polymeric structure is precipitated. However it should be noted that partial exchange is possible either through the use of an excess of the iso-propoxide or through immediate filtration of the reaction mixture. Both cases lead to a compound containing a mixture of methoxy and iso-propoxy ligands.

$$Al(O^iPr)_3 + xMeOH \longrightarrow Al(O^iPr)_{3-x}(OMe)_x + x^iPrOH$$

Thus it was essential to use an excess of methanol and to reflux the reaction mixture overnight to ensure complete reaction had occurred. The infra red spectrum of the product showed no evidence of residual iso-propoxide.

The preparation of copper(II) methoxide and zinc methoxide from the reaction of their chlorides with lithium methoxide demonstrates a standard method of preparing alkoxides[64,66,67]:

$$xLi(OR) + MCl_x \longrightarrow M(OR)_x + xLiCl$$

A problem that arises from this method is that of contamination of the product with chloride (typically 0.25%). Purification is possible only by washing with methanol or another suitable solvent, which is made difficult by the gelatinous nature of the products, as the methoxides are non-volatile and are insoluble in organic solvents.

It was for this reason that zinc methoxide was prepared using dialkylzinc species, the products obtained from these preparations being purer than those made using zinc chloride. The reaction between dialkylzincs and methanol was less vigorous than expected: having mixed the reagents in THF solutions at low temperature, warming to reflux was necessary to complete the reaction despite a safety handbook's[151] warning of an explosion risk! The reaction occurred in two stages: evolution of gas was observed on warming the reaction mixture to just below room temperarture, but warming was necessary to cause precipitation of the product and to push the reaction to completion. The two stage nature of this reaction was due to the formation of a cubane intermediate, RZnOMe[59,60]:

$$ZnR_2 + MeOH \longrightarrow RZnOMe + RH$$

$$RZnOMe + MeOH \longrightarrow Zn(OMe)_2 + RH$$

A low yield was obtained (40%) when using dimethylzinc compared to the yield obtained when using diethylzinc (94%). The dimethylzinc used was old, but was assumed to be reasonably pure as there was no precipitate of zinc hydroxide which would have been observed if hydrolysis had occurred to any great extent. An explanation for the low yield is that an error may have been made when measuring the volume (2ml) of dimethylzinc before dissolving it in THF. The diethylzinc used was supplied as a 1.1M toluene solution thus removing the possible error of measuring a very small volume of a pyrophoric liquid.

The preparation of copper(II) formate and zinc formate made use of the metal carbonates or basic carbonates in preference to the sulphate so as not to leave any potential poisons in the end product (sulphur is a common poison of copper based catalysts). e.g.

$$4HCO_2H + Cu(CO_3).Cu(OH)_2 + 5H_2O \longrightarrow 2Cu(O_2CH)_2.4H_2O + CO_2$$

Copper(II) formate, zinc formate, copper(II) acetate and zinc acetate (commercial samples of acetates) were all readily dehydrated by heating under vacuum.

5.2.2 Decompositions

The thermal decompositions were carried out in horizontal pyrolysis tubes heated by an electric furnace (for details see Appendix 1). In general terms, the copper compounds decomposed at lower temperatures than their zinc counterparts and the copper residues consisted of metallic copper whereas the zinc residues consisted of zinc metal, zinc oxide or a zinc oxy-salt. In some cases a simple reaction scheme may be written for the decompositions, whilst in others the decompositions were too complex. A summary of the results is given in Table 5.1.

Table 5.1 Summary of Decompositions

Compound	Temperature	Residue[1]	Volatile Products[2]
$Al(OMe)_3$	250 °C	Al_2O_3[3]	Me_2O, MeOH, $^{i}PrOH$
$Cu(OMe)_2$	160 °C	Cu	CO, CO_2, MeOH, MeO_2CH
$Zn(OMe)_2$	350 °C	Zn	CO, H_2, CO_2, Me_2O, MeOH, MeO_2CH
$Cu(O_2CH)_2$	200 °C	Cu	H_2, CO_2, HCO_2H
$Zn(O_2CH)_2$	290 °C	ZnO	CO, CO_2, MeO_2CH, H_2CO
$Cu(O_2CCH_3)_2$	220 °C	Cu	CO_2, HO_2CCH_3,
$Zn(O_2CCH_3)_2$	200 °C	$Zn_4O(OAc)_6$	HO_2CCH_3

Notes:

1. As determined by X-ray powder photograph.
2. As shown by ir and mass spectroscopy.
3. Determined by microanalysis.

The decomposition of aluminium methoxide resulted in the formation of alumina. The amounts of methanol and iso-propanol produced were small and, at least to some extent, can be accounted for by residual alcohol left after the product was dried. The main constituent of the volatiles produced was dimethyl ether. Thus:

$$2Al(OMe)_3 \xrightarrow{\Delta} Al_2O_3 + 3Me_2O$$

The decomposition of copper(II) methoxide resulted in the formation of copper metal (xrd). The volatiles were mainly methanol and methyl formate (molar ratio approx 2:1 by glc) with traces of carbon monoxide and carbon dioxide. Thus:

$$2Cu(OMe)_2 \xrightarrow{\Delta} 2Cu + 2MeOH + MeO_2CH$$

The decomposition of zinc methoxide led to the formation of a black collar, inside the pyrolysis tube, at the end of the furnace. Insufficient was collected for any analysis but it was presumed to be zinc metal. To sublime zinc metal at only 350°C was thought unlikely until a comparison of the relevant volatilities of zinc and mercury was made[144]: the vapour pressure of zinc at 350°C is similar to that of mercury at 25°C and a mirror of mercury is often observed in cold traps on an efficent vacuum line. The majority of the volatiles consisted of carbon monoxide and hydrogen (molar ratio approx. 1:2.5). Smaller quantities of methanol, carbon dioxide, dimethyl ether and methyl formate were detected (in order of quantity observed).

The decomposition of copper(II) formate was very interesting as a mirror of copper was formed at only 200°C indicating the presence of a volatile copper species. In one way this was disappointing as it had been hoped that structural features would be maintained during decomposition. The deposition of this copper onto ceramics, metals and glasses has been investigated[124] and the possibility of depositing copper from the vapour phase onto zinc oxide either pre-formed or formed in-situ was, however, interesting and formed the basis for much of the work described in chapter 6. The volatiles produced consisted of carbon dioxide, hydrogen and formic acid (approx molar ratio 5:2:1). Thus:

$$3Cu(O_2CH)_2 \xrightarrow{\Delta} 3Cu + 2H_2 + 5CO_2 + HCO_2H$$

It was thought that the volatile species involved in the above decomposition was copper(I) formate as it was reported[152] that it could be prepared in low (2%) yield by sublimation of copper(II) formate. Attempts to make some copper(I) formate in this way met with limited success: a white volatile species was isolated but in insufficient quantity for full characterisation, even when using a horizontal sublimation tube so the sublimate only had to travel 1.5cm to the cold finger. One interesting observation was the position of a copper mirror which formed on the walls of the sublimator during an experiment performed with a vertical sublimation apparatus heated with an oil bath. The mirror started to form level with the bottom of the cold finger, just below the top of the oil bath, some 8-10cm above the copper(II) formate. No copper metal was observed on the cold finger. This suggested that the volatile copper species sublimed to the walls of the vessel, which would be cooler near the top of the oil, before undergoing decomposition. Other volatile copper species are known, for example copper(I) acetate[153] and copper(II) nitrate[154].

The decomposition of zinc formate led to the formation of zinc oxide together with a complex mixture of volatiles. One point of interest was the formation of what was believed to be formaldehyde polymer identified by infra red (insufficient collected for microanalysis).

The decomposition of copper(II) acetate left a residue of copper metal and also a collar of a white crystalline substance believed to be copper(I) acetate which is known to be volatile at 200°C[153]. It was hydrolysed by water to yellow copper(I) oxide.

The decomposition of zinc acetate led to the formation of basic zinc acetate[155] whose thermal stability was not investigated. If it were to be investigated it would require the use of an inert gas stream as it is volatile at 210°C/0.01mm.

5.3 Experimental

5.3.1 Preparations

(a) Preparation of Aluminium Methoxide

To a solution of aluminium iso-propoxide (5.32g, 0.026mol, freshly distilled: 80-84°C/0.2 mm) in dry iso-propanol (80ml) was added dry methanol (10ml, 0.25mol) which led to the formation of a gelatinous white precipitate. The mixture was heated under reflux for 16 hours to ensure complete reaction, the mixture cooled, filtered (No.3 stick) and the white solid washed with dry methanol (2x20ml) before drying in vacuo. Yield 3.08g (98%). The product was characterised as follows:

Analysis	Found:	C,29.7; H,8.0; Al,21.5 %.
	$C_3H_9AlO_3$ Requires:	C,30.0; H,7.6; Al,22.5 %.

Infra Red (Nujol, cm^{-1}): 3000-2800, 1460, 1380(nujol); 1180(w); 1070(s); 580.

(b) Preparation of Copper(II) Methoxide

To dry methanol (180ml) was added, slowly with caution, lithium metal (1.00g, 0.144 mol). Once the evolution of hydrogen had ceased and the solution had cooled, a solution of anhydrous copper(II) chloride in dry methanol (110ml, 0.64M, 0.071mol) was added dropwise over a period of 1 hour affording, at first, a green precipitate which turned blue after half of the addition. The mixture was heated under reflux for 18 hours to increase the particle size, cooled and filtered (No.3 stick). The blue solid was washed with dry methanol (3x 20ml) and dried in vacuo. Yield 6.92g (76%). The product was characterised as follows:

Analysis Found: C,18.8; H,5.1; Cu,49.0 %.

$C_2H_6CuO_2$ Requires: C,19.1; H,4.8; Cu,50.6 %.

Infra Red (Nujol, cm^{-1}): 3000-2800(nujol); 2800(s,sh); 1460,
1375(nujol); 1150(sh); 1050(s);795(w); 720(w);
525(s); 440(s).

(c) Preparation of Zinc Methoxide

(i) Using Zinc Chloride

To dry methanol (100ml) was added, slowly with caution, lithium metal (0.54g, 0.078mol). Once the evolution of hydrogen had ceased and the solution had cooled, a solution of anhydrous zinc chloride in dry methanol (65ml, 0.58M, 0.038mol) was added dropwise over a period of 1 hour affording a granular white precipitate. The mixture was heated under reflux for 18 hours, cooled, filtered (No.2 stick) and the white solid washed with dry methanol (3x30ml) before drying in vacuo. Yield 3.00g (61%). The product was characterised as follows:

Analysis Found: C,17.7; H,4.4; Zn,51.7 %. (Cl <0.5%).

$C_2H_6O_2Zn$ Requires: C,18.9; H,4.8; Zn,51.3 %.

Infra Red (nujol, cm^{-1}): 3000-2800 (nujol); 2800 (s,sh); 1460, 1380 (nujol); 1045 (s); 720 (w); 485 (s).

(ii) Using Dimethylzinc

To a solution of dry methanol (10ml, 0.25mol) in dry THF (40ml) at -78°C was added, slowly with great caution, a solution of dimethylzinc (2ml, 0.029mol) in dry THF (20ml). A vigorous evolution of gas occurred on warming the mixture to -30°C and a slight cloudiness was apparent after stirring at room temperature for 1 hour. The mixture was heated under reflux for 18 hours, cooled, filtered (No.4 stick) and the white solid dried in vacuo. Yield 1.50g (40%). The product was characterised as follows:

Analysis Found: C,17.3; H,4.4; Zn,51.3 %.

$C_2H_6O_2Zn$ Requires: C,18.9; H,4.8; Zn,51.3 %.

Infra Red As above

(iii) Using Diethylzinc

To a solution of dry methanol (20ml, 0,494mol) in dry THF (60ml) at -15°C was added slowly with great caution a solution of diethylzinc in toluene (50ml, 1.1M, 0.055mol). A vigorous evolution of gas occurred followed by a clouding of the solution. The mixture was heated under reflux for 18 hours, cooled, filtered (No.4 stick) and the white solid dried in vacuo. Yield 6.61g (94%). The product was characterised as follows:

Analysis Found: C,18.2; H,4.3; Zn,51.1 %.

$C_2H_6O_2Zn$ Requires: C,18.9; H,4.8; Zn,51.3 %.

Infra Red As above.

(d) Preparation and Dehydration of Copper(II) Formate Tetrahydrate

To formic acid (100ml, 2M) was added basic copper(II) carbonate (5.7g, 0.052mol Cu) and the mixture was warmed and filtered hot. On cooling blue crystals formed which were separated by filtration. Yield 3.84g (33%). The product was characterised as follows:

Analysis Found: C,10.4; H,4.1; Cu,26.7 %.

$C_2H_{10}CuO_8$ Requires: C,10.7; H,4.5; Cu,28.2 %.

Infra Red (nujol, cm^{-1}): 3700-2500(br); 3000-2800(nujol); 1560(s,br); 1460(nujol); 1395; 1390(sh); 1375(nujol); 1320; 785; 600.

Copper(II) formate tetrahydrate (1.306g, 5.79mmol) was readily dehydrated by heating to 80°C under vacuum. A mass loss of 0.415g was observed (theoretical loss 0.417g) and the moisture sensitive material so produced was characterised as follows:

Analysis Found: C,16.0; H,1.3; Cu,41.2 %.

$C_2H_2CuO_4$ Requires: C,15.7; H,1.3; Cu,41.4 %.

Infra Red (nujol, cm^{-1}): 3000-2800(nujol); 1555(br); 1460, 1380(nujol); 1360; 830; 420.

(e) Preparation and Dehydration of Zinc Formate Dihydrate

This was prepared in the same way as copper(II) formate but using basic zinc carbonate. The white powder formed was characterised as follows:

<u>Analysis</u> Found: C,12.3; H,3.0; Zn,34.7 %.

$C_2H_6O_6Zn$ Requires: C,12.5; H,3.1; Zn,34.2 %.

<u>Infra Red</u> (nujol,cm^{-1}): 3650-2600(br); 3000-2800(nujol); 1665(sh); 1570(s,br); 1460(nujol); 1395(s); 1380(nujol); 1350(s); 875; 835; 760; 570.

Zinc formate dihydrate (8.212g, 0.0429mol) was dehydrated by heating to 80°C under vacuum. A mass loss of 1.56g was observed (theoretical loss 1.55g) and the moisture sensitive material so produced was characterised as follows:

<u>Analysis</u> Found: C,14.9; H,1.1; Zn,43.5 %.

$C_2H_2O_4Zn$ Requires: C,15.4; H.1.3; Zn,42.1 %.

<u>Infra Red</u> (nujol, cm^{-1}): 3150(w); 3000-2800(nujol); 2600(w); 1600(s,br); 1460, 1380(nujol); 1340; 810(s); 780(s).

(f) <u>Dehydration of Copper(II) Acetate Monohydrate</u>

Copper(II) acetate monohydrate (commercial sample) was readily dehydrated by heating to 120°C under vacuum for 2 hours. There was no change in its appearance and the product was characterised as follows:

<u>Analysis</u>: Found: C,26.8; H,3.5; Cu,34.7 %.

$C_4H_6CuO_4$ Requires: C,26.5, H,3.3; Cu,35.0 %.

<u>Infra Red</u> (nujol, cm^{-1}): 3000-2800(nujol); 1590(s); 1445(s,br); 1380(sh,nujol); 1350(sh); 1050; 945; 690(s); 625(s).

(g) Dehydration of Zinc Acetate Dihydrate

Zinc acetate dihydrate was also readily dehydrated by heating to 120°C under vacuum for 2 hours. There was no change in its appearance and the product was characterised as follows:

Analysis	Found:	C,25.8; H,3.3; Zn,37.1 %.
	$C_4H_6O_4Zn$ Requires:	C,26.2; H,3.3; Zn,35.6 %.

Infra Red (nujol, cm^{-1}): 3000-2800(nujol); 1600(sh); 1550(s); 1450(s,br); 1380(sh); 1050(sh); 1030(s); 955(s); 700(s) 690(sh); 610(s); 520.

5.3.2 Thermal Decompositions

(a) Decomposition of Aluminium Methoxide

Aluminium methoxide (0.22g, 1.83mmol) was placed in a pyrex boat which was then inserted into a pyrolysis tube and heated to 200°C for 2 hours under a stream of dry nitrogen. A small quantity (0.36mmol) of methanol and iso-propanol were evolved (ir). Heating to 350°C for 5 hours gave rise to a further small quantity (0.44mmol) of methanol and a much larger quantity (2.21mmol) of dimethylether, the mixture being separated by fractionating between a liquid nitrogen cooled trap and one cooled by an acetone/dry ice slush bath. The residue was mainly alumina:

Analysis	Found:	C,0.4; H,1.0; Al,51.1 %.
	Al_2O_3 Requires:	C,0.0; H,0.0; Al,52.9 %.

(b) Decomposition of Copper(II) Methoxide

Copper(II) methoxide (0.718g, 5.71mmol) was placed in a pyrolyis tube, the tube evacuated and weighed (113.503g). The tube was then heated in a static vacuum to 115°C for 2 hours with little effect. The temperature was raised to 160°C and maintained for a further 2 hours during which time the solid went a red/brown colour. The small quantity of non-condensable volatiles produced was shown to contain carbon monoxide (ir). The much greater (ca 10 times) quantity of condensable volatiles was shown to consist of a small amount of carbon dioxide (liquid nitrogen fraction) together with a mixture of methanol and methyl formate (acetone/dry ice fraction, approximately 2:1 by glc and ^{1}H nmr). A mass loss of 0.344g was observed (theoretical if residue copper metal, 0.355g. The residue contained no carbon or hydrogen and was 92.3% copper. An x-ray powder photograph showed copper metal to be present.

(c) Decomposition of Zinc Methoxide

Zinc methoxide (0.569g, 4.46mmol) was placed in a pyrolysis tube, the tube evacuated and weighed (104.525g). The tube was then heated in a static vacuum to 250°C with little effect save for the formation of a black collar just outside the heated region of the tube. The temperature was raised to 350°C and maintained for 2 hours producing a large quantity of non-condensable volatiles (8.7 mmol) estimated to contain carbon monoxide (ir) and hydrogen (ms) in the ratio 1:2.5 (by molecular weight determination). The smaller quantity of condensable volatiles contained carbon dioxide and dimethyl ether (liquid nitrogen fraction, 1.34mmol) and methyl formate and methanol (acetone/dry ice fraction, 0.34mmol). A mass loss of 0.248g was observed (theoretical if residue zinc metal, 0.277g; zinc oxide 0.206g). The residue contained a small amount of carbon (1.77%) no hydrogen and 95.37% zinc. An x-ray powder photograph showed zinc metal to be present, no lines for zinc oxide were observed.

(d) Decomposition of Copper(II) Formate

(i) In standard pyrolysis tube

Copper(II) formate (0.475g, 3.10mmol) was placed in a pyrolysis tube, the tube evacuated and weighed (106.279g). The tube was then heated in a static vacuum to 200°C producing a mirror of copper on the inside of the pyrolysis tube, non-condensable volatiles (1.86mmol) assumed to be hydrogen (no CO in ir) and condensable volatiles consisting of carbon dioxide (liquid nitrogen fraction, 5.15mmol) and formic acid (acetone/dry ice fraction, 1.06mmol). A mass loss of 0.281g was observed (theoretical if residue copper metal, 0.279g). Analysis of the residue showed it to be 100% copper which was confirmed by an x-ray powder photograph

(ii) In a sublimator

Copper(II) formate was placed in the bottom of a sublimator and the sublimator evacuated. When a vacuum of better than 0.01mm had been achieved the sublimator was heated, using an oil bath, to 135°C, at which point a faint cloudiness was observed on the cold finger. At 140°C this became more pronounced and a copper mirror started to form on the walls of the sublimator, level with the bottom of the cold finger just below the top of the oil bath. The temperature was further increased to 190°C but the amount of sublimate did not increase and insufficient was collected for analysis.

In an attempt to collect sufficient material for analysis, the sublimation was repeated, using an electric furnace in a horizontal position so that the distance between the copper formate and the cold finger of the sublimation apparatus was much smaller than above. Copper(II) formate (3.683g, 0.024mol) was placed in a sublimator, the sublimator inserted into the furnace and evacuated. When a vacuum of better than 0.01mm had been achieved the temperature was raised to 135°C and maintained for 12 hours, during which time the copper formate darkened, a slight copper mirror formed and a white solid was deposited on the cold finger. Qualitative analysis showed this to contain copper and an infra red spectrum was recorded as a KBr disc which was prepared in air:

(cm^{-1}) 3700-3100; 2920(w); 2840; 2700(w); 1620(s); 1385(sh); 1355(sh); 1325(s); 1100(w); 1025(w); 910(w); 865(w); 785(s); 780(s); 620(w); 525(w); 450; 405; 340.

(e) Decomposition of Zinc Formate

Zinc formate (0.827g, 5.32mmol) was placed in a pyrolysis tube, the tube evacuated and weighed (115.088g). The tube was then heated to 290°C for 1½ hours producing non-condensable volatiles (3.63mmol) shown to contain carbon monoxide (ir) together with condensable volatiles containing carbon dioxide (liquid nitrogen fraction, 4.67mmol) and methyl formate (acetone/dry ice fraction, 1.01mmol). A white solid was observed in the cold trap which was thought to be formaldehyde polymer (ir). A mass loss of 0.393g was observed (theoretical if residue zinc oxide, 0.394g). The residue contained a small amount of carbon (0.83%) and hydrogen (0.14%) and was 81.50% zinc (ZnO requires 80.33%). An x-ray powder photograph showed zinc oxide to be present.

(f) Decomposition of Copper(II) Acetate

Copper(II) acetate (1.850g,0.0 102mol) was placed in a pyrolysis tube and the tube evacuated and heated to 220°C for 8 hours. A large quantity of volatiles was produced which contained carbon dioxide, acetic acid and a trace of acetic anhydride (ir). A collar of an off white crystalline material was observed at the end of the furnace which was assumed to be copper(I) acetate[153] as it was hydrolysed by water to yellow copper(I) oxide. The main portion of the residue contained no carbon or hydrogen and was 97.89% copper. An x-ray powder photograph showed copper metal to be present.

(g) Decomposition of Zinc Acetate

Zinc acetate (0.83g, 4.5mmol) was placed in a pyrolysis tube and the tube heated to 200°C under a stream of dry nitrogen. A small quantity of acetic acid (ir) was given off and a sublimate of a white crystalline compound was formed on the nitrogen inlet tube (insufficient for analysis). The sublimate was thought to be basic zinc acetate: $Zn_4O(OCOCH_3)_6$[155] a sample of which was prepared by heating a portion of zinc acetate to 210°C in a sublimator (0.01mm). The white product collected was characterised as follows:

Analysis Found: C,22.6; H,2.7; Zn,41.8 %.

$C_{12}H_{18}O_{13}Zn_4$ Requires: C,22.8; H,2.9; Zn,41.4 % .

Infra Red (nujol, cm^{-1}): 3000-2800(nujol); 1600(sh); 1550(s,) 1450(s,br); 1380(sh); 1050(sh); 1030(s); 955(s); 665(s) 690(sh); 610(s); 520.

The residue from the original decompoosition consisted of a mixture of zinc acetate and basic zinc acetate:

Analysis Found: C,25.5; H,3.1; Zn,37.5 %.

$C_4H_6O_4Zn$ Requires: C,26.2; H,3.3; Zn,35.6 %.

$C_{12}H_{18}O_{13}Zn_4$ Requires: C,22.8; H,2.9; Zn,41.4 %.

Infra Red Sum of spectra of Zinc Acetate and Basic Zinc Acetate.

CHAPTER 6

Thermal Decompositions of Mixtures of Alkoxides and Carboxylates

6.1 Introduction

This chapter describes the thermal decompositions of mixtures of an alkoxide of one metal with a carboxylate of another which were carried out to see whether ester elimination would occur generating a mixed metal oxide:

$$M^1\text{-}OR \;+\; M^2\text{-}O_2CR' \xrightarrow{\Delta} M^1\text{-}O\text{-}M^2 \;+\; RO_2CR'$$

The materials produced by such decompositions of copper(II) formate with zinc methoxide or zinc oxide were evaluated as catalysts. A discussion of the decompositions and the characterisation of the residues so produced is followed by the experimental details.

6.2 Discussion

6.2.1 Decompositions

The mixed decompositions described in this chapter (see Table 6.1 overleaf for summary) can be compared to the thermal decompositions of the individual components which were all described in the previous chapter (see Table 5.1, page 79). This comparison of volatile products and solid residues gave evidence which supported the above hypothesis in all of the mixed decompositions described.

Table 6.1 Summary of Mixed Decompositions

Compounds	Temperature	Conditions	Residue[1]	Volatile Products[2]
$Al(OMe)_3$ $Cu(O_2CCH_3)_2$	250 °C	vacuum	–[3]	MeO_2CMe, MeOH, CO_2, $MeCO_2H$
$Al(OMe)_3$ $Zn(O_2CCH_3)_2$	220 °C	N_2 stream	–[3]	MeO_2CMe, MeOH CO_2, $MeCO_2H$
$Zn(OMe)_2$ $Cu(O_2CH)_2$	250 °C	static vacuum	Cu/ZnO	CO, H_2, CO_2, MeOH, MeO_2CH
"	250 °C	vacuum	Cu/ZnO	CO_2, MeOH, MeO_2CH
"	325 °C	N_2/H_2 stream	Cu/ZnO	CO_2, MeOH, MeO_2CH
"	325 °C	0.1atm N_2/H_2	Cu/ZnO	CO_2, MeOH, MeO_2CH
"	230 °C	N_2 then N_2/H_2	Cu/ZnO	CO_2, MeOH, MeO_2CH
ZnO $Cu(O_2CH)_2$	250 °C	static vacuum	Cu/ZnO	CO, H_2, CO_2, H_2O, MeO_2CH
"	325 °C	vacuum	Cu/ZnO	CO_2, MeO_2CH, HCO_2H
"	325 °C	N_2/H_2 stream	Cu/ZnO	CO_2, MeOH, HCO_2H, MeO_2CH
"	325 °C	0.1atm N_2/H_2	Cu/ZnO	CO_2, H_2O, HCO_2H
"	230 °C	N_2 then N_2/H_2	Cu/ZnO	CO_2, MeOH, HCO_2H, MeO_2CH
$Cu(OMe)_2$ $Zn(O_2CH)_2$	350 °C	static vacuum	–[3]	CO, CO_2, MeOH, MeO_2CH

Notes:

1. As determined by X-ray powder photograph.
2. As shown by ir and mass spectroscopy.
3. Incomplete decompositions.

(a) Decompositions of Aluminum Methoxide with Copper(II) and Zinc Acetates

The decompositions of aluminium methoxide with copper(II) or zinc acetates showed significant differences from the individual decompositions in that methyl acetate was evolved and no dimethyl ether was evolved which was the major product in the decomposition of aluminium methoxide. The incomplete nature of these decompositions, there being 10% carbon in the residues (mainly carboxylate, from ir), led to the use of simpler carboxylates in subsequent decompositions (i.e formate not acetate). A further change was made in that the decompositions described below involve compounds of copper and zinc but not aluminium as it is generally assumed that the aluminium component of the industrial catalyst acts merely as a support[16].

(b) Decompositions of Zinc Methoxide with Copper(II) Formate

A series of decompositions of zinc methoxide with copper(II) formate were carried out under various conditions to see whether they affected the products. As can be seen from the data in Table 6.1 the conditions employed did not appear to affect the nature of the volatiles or the chemical nature of the residue. However the conditions did affect the physical nature of the residue (see section 6.2.2). There are three major differences between the mixed decomposition when compared to the individual decompositions: no copper mirror was observed; zinc oxide was produced rather than zinc metal and a significant quantity (approximately 25% yield) of methyl formate was produced.

(c) Decompositions of Zinc Oxide with Copper(II) Formate

A series of decompositions of mixtures of zinc oxide and copper(II) formate were carried out under similar conditions to those used for the decompositions of zinc methoxide with copper(II) formate to see whether the residues were the same. The residues again consisted of copper metal and zinc oxide and their physical nature was also affected by the conditions employed (see section 6.2.2). In this case the nature of the volatiles was affected by the conditions employed as in two cases (N_2/H_2 stream and N_2 then N_2/H_2 stream) methanol was detected in the volatiles. The fact that no copper mirror was observed in this decomposition may indicate that the absence of such a mirror in the decomposition of copper(II) formate with zinc methoxide was not due to any chemical reaction but due to the availability of a large surface area of a support material on to which the copper may have been deposited. The evolution of methyl formate may be due to the formation and subsequent decomposition of zinc formate (from the reaction of zinc oxide with formic acid produced in the decomposition of copper(II) formate).

(d) Decomposition of Copper(II) Methoxide with Zinc Formate

The decomposition of copper(II) methoxide with zinc formate did not have any major differences from the individual decompositions. The residue was obviously inhomogeneous, consisting of a dark coloured powder with white particles in it and therefore was not further investigated.

6.2.2 Evaluation of Materials as Catalysts

The materials produced by the thermal decomposition of mixtures of copper(II) formate with zinc methoxide and zinc oxide were evaluated as catalysts. The materials were identified as copper metal/zinc oxide mixtures by microanalysis and x-ray powder diffraction but this gave no information as to the surface properties of the materials and thus their potential as catalysts. Therefore the materials were further characterised using the following techniques.

(a) X-Ray Photoelectron Spectroscopy

The use of x-ray photoelectron spectroscopy (XPS) confirmed the presence of copper metal and zinc oxide in the residues. However it also showed that the copper was not very finely divided as only a weak signal was obtained for the copper binding energy which is indicative of the copper having sintered.

(b) Transmission Electron Microscopy

A second technique that is useful in ascertaining the size of the copper particles is that of transmission electron microscopy. Thus, series of electron micrographs were obtained of the residues and a comparison of these indicated that the optimum conditions for producing small copper particles was heating to 230°C in nitrogen followed by reduction in N_2/H_2 also at 230°C. Typical micrographs of these residues are contained in the experimental section of this chapter. Larger copper particles were observed for the residues produced at higher temperatures and under more severe conditions.

The micrographs of the residues produced under the optimum conditions clearly show differences between that produced from zinc methoxide and that from zinc oxide. The residue produced from the methoxide appears to have a more open structure and to consist of smaller particles of copper than that produced from the oxide. This difference should lead to a larger copper surface area and thus higher activity. Indeed an estimate of the copper surface area from the micrographs gives surface areas of approximately $48m^2g^{-1}$ and $14m^2g^{-1}$ for the residues from methoxide and oxide respectively. These figures assume that the copper particles are spherical and also that the sample used for the electron micrograph was representative of the whole. This last assumption is probably invalid as the technique employed to prepare the sample (one or two drops of an ethanol suspension of the material dropped on to an aluminium grid) would tend to select the lighter and therefore smaller particles. Therefore the surface area estimates above are likely to be higher than the actual surface area.

(c) Copper Surface Area Determination

The surface area of the copper in the materials was determined by its reaction with nitrous oxide which generates copper(I) oxide and nitrogen. These measurements were all carried out at the Catalysis Research Centre, Billingham by ICI personnel. All of the materials which were measured had surface areas less than $0.5m^2g^{-1}$ which was very disappointing as commercial catalysts typically have areas of $30\text{-}40m^2g^{-1}$. It was thought that the copper may have "balled up" on exposure to air between the decomposition and the surface area measurement so surface area determinations were carried out on two samples which were decomposed in the apparatus used to measure the areas. However these also had surface areas less than $0.5m^2g^{-1}$. These figures show that the samples used for the transmission electron microscopy were not representative of the whole: in addition to the finely divided copper observed there must have been a significant amount of sintered copper of much larger particle size.

(d) Catalyst Activity Tests

The activity of two samples which were decomposed in nitrogen at 230°C followed by reduction (N_2/H_2) at 230°C were determined relative to a standard industrial catalyst using a microreactor. These measurements were also recorded at the Catalysis Research Centre, Billingham by ICI personnel. The residue from zinc oxide/copper(II) formate had a relative activity of 2% whilst the residue from zinc methoxide/copper(II) formate had a relative activity of 7%. The latter figure, although small, is interesting as from the very low surface areas recorded it was expected that the material would be inactive. Thus it appears that there is some copper present that is active but that is not detected by the nitrous oxide reaction.

6.2.3 Summary

The work described in this chapter shows that the thermal decomposition of mixtures of alkoxides and carboxylates are generally very different to the decomposition of the individual components. The materials obtained from the decomposition of copper(II) formate and either zinc methoxide or zinc oxide were copper metal/zinc oxide and appeared to consist, at least partially, of very small particles of copper (TEM). However they had immeasurably small copper surface areas as determined by nitrous oxide titration indicating that significant sintering had probably occurred during the decomposition. Nonetheless they did show some activity for the production of methanol from syngas. The sintering may be reduced if the decomposition were to be carried out in an oxidising atmosphere and then the residue slowly reduced in N_2/H_2 but this was not investigated.

6.3 Experimental

6.3.1 Decomposition of Aluminium Methoxide with Copper(II) and Zinc Acetates

(a) With Copper(II) Acetate

A finely ground mixture of aluminium methoxide (0.170g, 1.416mmol) and anhydrous copper(II) acetate (0.390g, 2.147mmol) was placed in a pyrolysis tube, the tube evacuated, weighed (242.20g) and then heated, under a dynamic vacuum, to 250°C for 6 hours. A large quantity of volatiles was evolved, which consisted of a mixture of methyl acetate, methanol, carbon dioxide and a trace of acetic acid. A mass loss of 0.20g was observed (theoretical if residue $Al_2Cu_3O_3$, 0.35g). The residue was characterised as folows:

<u>Analysis</u> Found: C,10.9; H,1.3; Al,15.6; Cu,49.8 %

$Al_2O_3Zn_3$ Req: C,0.0; H,0.0; Al,18.4; Cu,65.2 %

<u>Infra Red</u> (Nujol, cm^{-1}): 3000-2800(nujol); 1600(br); 1460,1380(nujol).

(b) With Zinc Acetate

A finely ground mixture of aluminium methoxide (0.25g, 2.08mmol) and anhydrous zinc acetate (0.57g, 3.12mmol) was placed in a pyrolysis tube and the tube heated to 140°C for 3 hours under a stream of dry nitrogen producing a small quantity of methanol. The temperature was then raised to 220°C and maintained for 86 hours producing volatiles which consisted of a mixture of methyl acetate, methanol, acetic acid and acetone. A mass loss of 0.32g was observed (theoretical loss if residue is $Al_2Zn_3O_6$, 0.46g). The residue was characterised as follows:

<u>Analysis</u> Found: C,8.5; H,1.6; Al,11.5; Zn,48.9 %

$Al_2O_6Zn_3$ Req: C,0.0; H,0.0; Al,15.6; Zn,56.7 %

<u>Infra Red</u> (Nujol, cm^{-1}): 3000-2800(nujol); 1600(br); 1460,1380(nujol).

6.3.2 Decompositions of Zinc Methoxide and Copper(II) Formate

Series of decompositions were carried out of finely ground mixtures of zinc methoxide and copper(II) formate under various conditions:

(a) Under a Static Vacuum

A finely ground mixture of zinc methoxide (0.610g, 4.79mmol) and anhydrous copper(II) formate (0.733g, 4.77mmol) was placed in a pyrolysis tube, the tube evacuated, weighed (119.996g) and heated, under a static vacuum, to 250°C for 3 hours. The powder turned a brown/red colour and non-condensable volatiles were produced (6.9mmol) estimated to contain carbon monoxide (ir) and hydrogen (ms) in the ratio 1:1 (by molecular weight determination). The larger quantity of condensable volatiles produced contained carbon dioxide (liquid nitrogen fraction, 4.3mmol) and methyl formate and methanol (methanol/liquid nitrogen fraction, 0.312g, approx. 1:1 by glc: 3.4mmol of each). A mass loss of 0.605g was observed (theoretical if residue Cu/ZnO, 0.650g). An x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

<u>Analysis</u>	Found:	C,0.9; H,0.3; Cu,44.6; Zn,42.8 %
	CuOZn Req:	C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

(b) <u>Under Dynamic Vacuum</u>

A finely ground mixture of zinc methoxide (2.200g, 0.0173mol) and anhydrous copper(II) formate (2.630g, 0.0171mol) was placed in a pyrolysis tube, the tube evacuated, weighed (121.930g) and heated, under a dynamic vacuum, to 250°C for 3 hours. At 200°C a vigorous decomposition occurred, blowing some of the powder out of the pyrolysis tube into the sinter which was being used to protect the vacuum line, thus rendering mass loss measurements worthless. The powder turned a brown/red colour and condensable volatiles were produced which contained carbon dioxide, methyl formate and methanol. Further heating to 325°C for 2 hours produced only a small quantity of carbon dioxide and methanol; there was evidence that non-condensable volatiles had been produced as the vacuum fell to 0.5mm returning to 0.01mm after an hour without any adjustment to the vacuum line. A grey collar was also observed just outside the heated region of the pyrolysis tube. An x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

Analysis Found: C,0.4; H,0.0; Cu,40.0; Zn,49.4 %

CuOZn Req: C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

(c) Under a Stream of Nitrogen/Hydrogen (75:25)

A finely ground mixture of zinc methoxide (2.198g, 0.0173mol) and anhydrous copper(II) formate (2.649g, 0.0173mol) was placed in a pyrolysis tube, the tube evacuated and weighed (263.08g). A stream of nitrogen/hydrogen (75:25) was passed over the powder (c.a. 3ml per second) and the temperature raised to 200°C. The powder turned a brown/red colour and some of the volatiles produced condensed just outside the heated region of the pyrolysis tube which were removed by temporarily increasing the gas flow. The temperature was increased to 325°C and maintained for 2 hours producing a further quantity of volatiles. The volatiles consisted of carbon dioxide, methyl formate and methanol. A mass loss of 2.37g was observed (theoretical if residue Cu/ZnO, 2.35g). The residue did not appear as homogeneous (microscope) as those from vacuum decompositions. However an x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

Analysis Found: C,0.0; H,0.0; Cu,42.7; Zn,45.0 %

CuOZn Req: C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

(d) Under Reduced Pressure Stream of Nitrogen/Hydrogen (75:25)

A finely ground mixture of zinc methoxide (1.550g, 0.0122mol) and anhydrous copper(II) formate (1.867g, 0.0122mol) was placed in a pyrolysis tube, the tube evacuated and weighed (261.86g). A stream of nitrogen/hydrogen (75:25) was passed over the powder at approximately 0.1atm pressure; the pressure and flow rates were adjusted by means of a needle valve on the inlet and a high vacuum tap on the outlet of the pyrolysis system. A flow rate of approximately 5ml per second was used. The temperature was then raised to 200°C causing the powder to turn a brown/red colour and evolving a large quantity of volatiles. The temperature was increased to 325°C and maintained for 1 hour producing a further quantity of volatiles. The volatiles consisted of carbon dioxide, methyl formate and methanol. A mass loss of 1.62g was observed (theoretical if residue Cu/ZnO, 1.66g). An x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

<u>Analysis</u>	Found:	C,0.3; H,0.0; Cu,40.7; Zn,44.8 %
	CuOZn Req:	C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

(e) <u>Under a Stream of Nitrogen followed by Reduction Under a Stream of Nitrogen/Hydrogen (75:25)</u>

A finely ground mixture of zinc methoxide (1.322g, 0.0104mol) and anhydrous copper(II) formate (1.595g, 0.0104mol) was placed in a pyrolysis tube, the tube evacuated and weighed (261.41g). A stream of nitrogen was passed over the powder and the temperature was raised to 230°C and maintained for 4 hours. The powder turned a dark red/brown colour and a large quantity of volatiles was given off which consisted of a mixture of carbon dioxide, methyl formate and methanol. The gas stream was then altered to nitrogen/hydrogen (75:25) and a temperature of 230°C maintained for a further 4 hours during which time water was evolved (ir). A mass loss of 1.37g was observed (theoretical if residue Cu/ZnO, 1.41g). An x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

<u>Analysis</u>	Found:	C,1.9; H,0.3; Cu,43.3; Zn,41.9 %
	CuOZn Req:	C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

6.3.3 <u>Decompositions of Zinc Oxide and Copper(II) Formate</u>

Series of decompositions were carried out of finely ground mixtures of zinc oxide and copper(II) formate under various conditions:

(a) <u>Under a Static Vacuum</u>

A finely ground mixture of zinc oxide (1.407g, 0.0173mol) and anhydrous copper(II) formate (2.830g, 0.0184mol) was placed in a pyrolysis tube, the tube evacuated, weighed (116.119g) and heated, under a static vacuum, to 200°C for 2 hours. This caused the evolution of a large quantity of both non-condensable and condensable volatiles and the powder turned a grey/red colour. On raising the temperature to 250°C further volatiles were produced and the powder turned grey in colour. This temperature was maintained for 2 hours. The non-condensable volatiles produced (10.22mmol), were shown to contain carbon monoxide (ir) and assumed to contain hydrogen (absorptions in ir too small for given pressure for gas to be neat carbon monoxide, no evidence for air leak). The larger quantity of condensable volatiles produced contained carbon dioxide (liquid nitrogen fraction, 9.58mmol) methyl formate and water (methanol/liquid nitrogen fraction, 1.016g). A mass loss of 1.591g was observed (theoretical if residue Cu/ZnO, 1.660g). An x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

Analysis Found: C,0.0; H,0.0; Cu,45.7; Zn,45.2 %

CuOZn Req: C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

(b) Under Dynamic Vacuum

A finely ground mixture of zinc oxide (1.403g, 0.0172mol) and anhydrous copper(II) formate (2.647g, 0.0172mol) was placed in a pyrolysis tube, the tube evacuated, weighed (113.117g) and heated, under a dynamic vacuum, slowly raising the temperature to 325°C which was maintained for 3 hours. Above 225°C little decomposition occurred. The powder turned a red/grey colour and condensable volatiles were produced which contained carbon dioxide, methyl formate and formic acid. A mass loss of 1.483g was observed (theoretical if residue Cu/ZnO, 1.552g). An x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

Analysis Found: C,0.0; H,0.0; Cu,43.0; Zn,44.7 %

CuOZn Req: C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

(c) Under a Stream of Nitrogen/Hydrogen (75:25)

A finely ground mixture of zinc oxide (1.401g, 0.0172mol) and anhydrous copper(II) formate (2.649g, 0.0173mol) was placed in a pyrolysis tube, the tube evacuated and weighed (262.20g). A stream of nitrogen/hydrogen (75:25) was passed over the powder (c.a. 3ml per second) and the temperature gradually raised to 325°C and maintained for 2 hours. The powder turned a red/grey colour and condensable volatiles were produced which contained carbon dioxide, methyl formate, methanol and formic acid. A mass loss of 1.52g was observed (theoretical if residue Cu/ZnO, 1.56g). An x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

Analysis Found: C,0.0; H,0.0; Cu,42.9; Zn,45.6 %

CuOZn Req: C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

(d) Under Reduced Pressure Stream of Nitrogen/Hydrogen (75:25)

A finely ground mixture of zinc oxide (1.404g, 0.0173mol) and anhydrous copper(II) formate (2.649g, 0.0173mol) was placed in a pyrolysis tube, the tube evacuated and weighed (262.80g). A stream of nitrogen/hydrogen (75:25) was passed over the powder at approximately 0.1atm pressure; the pressure and flow rates were adjusted by means of a needle valve on the inlet and a high vacuum tap on the outlet of the pyrolysis system. A flow rate of approximately 5ml per second was used. The temperature was then raised gradually to 325°C producing condensable volatiles which consisted of carbon dioxide, water and a trace of formic acid. The powder turned a red/brown colour at 200°C turning a red/grey colour at 250°C. A mass loss of 1.47g was observed (theoretical if residue Cu/ZnO, 1.55g). An x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

Analysis Found: C,0.0; H,0.0; Cu,44.8; Zn,43.7 %

CuOZn Req: C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

(e) Under a Stream of Nitrogen followed by Reduction Under a Stream of Nitrogen/Hydrogen (75:25)

A finely ground mixture of zinc oxide (1.341g, 0.0165mol) and anhydrous copper(II) formate (2.531g, 0.0165mol) was placed in a pyrolysis tube, the tube evacuated and weighed (262.83g). A stream of nitrogen was passed over the powder and the temperature was raised to 230°C and maintained for 4 hours. The powder turned a red/brown colour and a large quantity of volatiles were given off which consisted of a mixture of carbon dioxide, methyl formate, methanol and formic acid. The gas stream was then altered to nitrogen/hydrogen (75:25) and a temperature of 230°C maintained for a further 2 hours during which time water was evolved (ir). A mass loss of 1.45g was observed (theoretical if residue Cu/ZnO, 1.48g). An x-ray powder photograph confirmed the presence of copper metal and zinc oxide in the residue, which was analysed:

Analysis	Found:	C,0.0; H,0.0; Cu,46.3; Zn,45.8 %
	CuOZn Req:	C,0.0; H,0.0; Cu,43.9; Zn,45.1 %

6.3.4 Decomposition of Copper(II) Methoxide and Zinc Formate

A finely ground mixture of copper(II) methoxide (0.429g, 3.41mmol) and anhydrous zinc formate (0.538g, 3.46mmol) was placed in a pyrolysis tube, the tube evacuated, weighed (109.848g) and then heated, under a static vacuum, to 170°C for 6 hours during which time the solid turned a brown/red colour. Both non-condensable and condensable volatiles were produced which were combined with the smaller quantity of volatiles produced when the temperature was slowly raised (over a period of 2 hours) to 350°C and maintained for 2 hours. These volatiles contained carbon monoxide (non-condensable, 2.14mmol), carbon dioxide (liquid nitrogen fraction, 2.46mmol) and methanol and methyl formate (acetone/dry ice fraction, approx 1:1 by glc, 2.62mmol of each). The figure for carbon monoxide assumes that no hydrogen was evolved, a molecular weight determination would be necessary to check this. A mass loss of 0.409g was recorded (theoretical if residue Cu/ZnO, 0.470g). The residue which was speckled in appearance consisted of copper (39.3%) and zinc (45.7%) with a small amount of residual organic contamination (2% carbon).

6.3.5 Evaluation of Materials as Catalysts

(a) X-Ray Photoelectron Spectroscopy

XPS were recorded for several of the residues from the decompositions of copper(II) formate with zinc methoxide or zinc oxide. These all confirmed the presence of copper metal (binding energy observed 932.2eV lit[156], 932.7eV) and zinc oxide (binding energy observed 1022.3eV lit[156], 1022.0eV). The zinc oxide peak was much more intense than that for copper metal even when the sensitivity factors were taken into account.

(b) Transmission Electron Microscopy

Transmission electron micrographs were taken of several of the residues from the decomposition of copper(II) formate with zinc methoxide or zinc oxide. These showed that smaller particles resulted when the decompositions were carried out at 230°C under a stream of nitrogen followed by reduction also at 230°C under a stream of nitrogen/hydrogen (75:25). Typical micrographs of two such residues are included overleaf. They show that the residue from the methoxide is more finely divided than that from the oxide. Estimates of the surface areas may be made: from the oxide $14m^2g^{-1}$, assuming average particle size of 23.8nm (10mm on micrograph) and from the methoxide $48m^2g^{-1}$, assuming average particle size of 7.0nm (3mm on micrograph).

The transmission electron micrographs overleaf are of:

TOP: Residue from Decomposition of Zinc Oxide with Copper(II) Formate

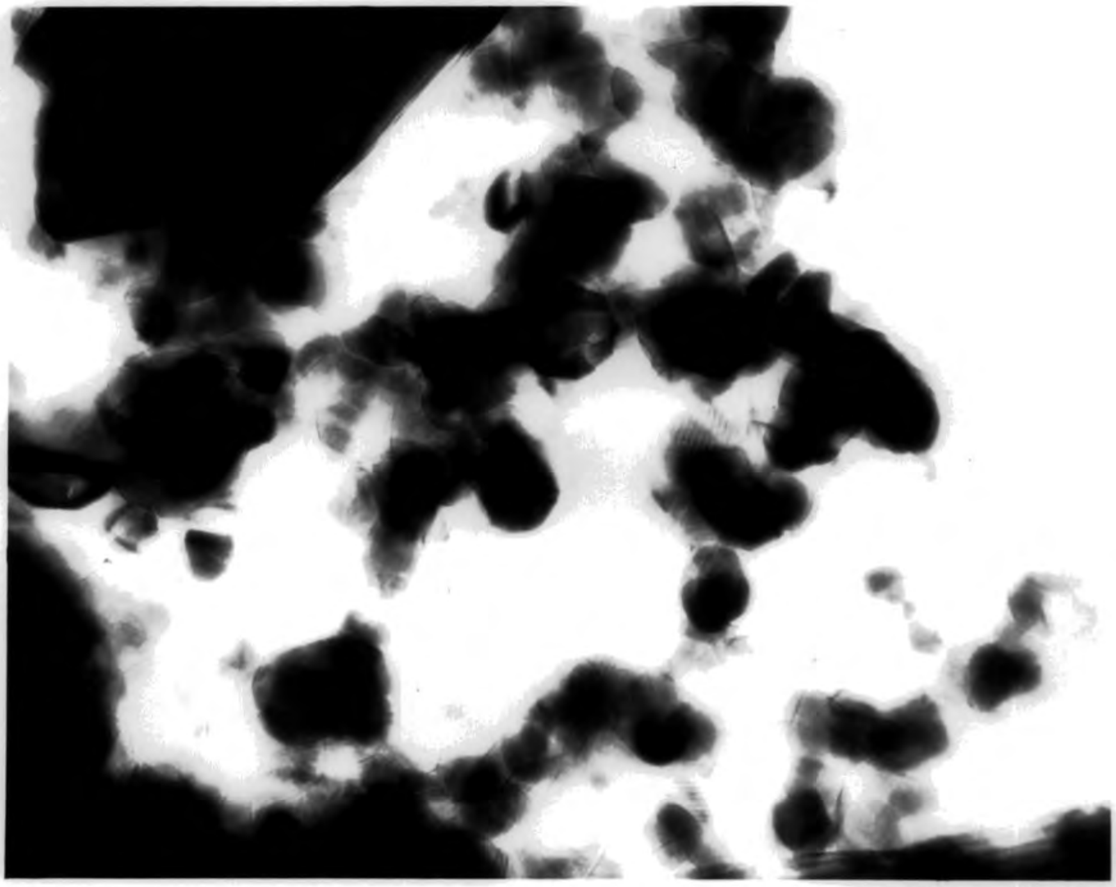
Conditions: N_2 stream at 230°C followed by N_2/H_2 stream at 230°C.

Magnification: 420 000, 1cm represents 23.8nm

BOTTOM: Residue from Decomposition of Zinc Methoxide with Copper(II) Formate

Conditions: N_2 stream at 230°C followed by N_2/H_2 stream at 230°C.

Magnification: 430 000, 1cm represents 23.3nm



(c) Copper Surface Area

The copper surface areas of the residues produced from copper(II) formate and zinc methoxide or zinc oxide were measured by ICI personnel at the Catalysis Research Centre, Billingham. The technique used was that of nitrous oxide titration in which surface copper reacts with N_2O producing copper(I) oxide with measurements of the nitrogen evolved being made using a katharometer and a mass spectrometer:[157]

$$2Cu + N_2O \longrightarrow Cu_2O + N_2$$

All surface areas were less than $0.5 m^2 g^{-1}$, even for samples decomposed in the apparatus used for the measurements.

(d) Catalyst Activity Measurements

Despite the low copper surface areas, activities of the residues from the decompositions at 230°C under a stream of nitrogen followed by nitrogen/hydrogen (75:25) were evaluated relative to a standard industrial catalyst using a microreactor. These measurements were also made at the Catalysis Research Centre, Billingham by ICI personnel. The residue from copper(II) formate and zinc oxide had a relative activity of 2% whilst that from copper(II) formate and zinc methoxide had a relative activity of 7%.

CHAPTER 7

Preparation of Mixed Metal Alkoxycarboxylates of Copper and Zinc

7.1 Introduction

This chapter describes the preparation of various soluble alkoxides and hydroxycarboxylates of copper and zinc. It then goes on to describe reactions between such species which were carried out in attempts to prepare mixed metal compounds of copper and zinc. Finally, preliminary studies on their impregnation onto alumina extrudate, subsequent decomposition and catalytic evaluation is reported. A discussion of the work is followed by the experimental details.

7.2 Discussion

The work described in this chapter was based on a very simple methodology: that of the reaction of an acid and a base to give a salt. In this case the acid of the system was the hydroxyl group of a metal hydroxycarboxylate and the base was an alkoxide of a different metal. i.e.

7.2.1 Preparation of Alkoxides

The number of known alkoxides of copper and zinc which are soluble in organic solvents is very small. The simple alkoxides such as the methoxide, ethoxide and iso-propoxide are all very insoluble due to their polymeric nature, a point which has already been alluded to in chapter 5. However there are a few which are soluble and these were prepared, mostly according to the literature with in some cases modifications or innovations being made to the reported procedures.

In addition, the preparation of a new soluble zinc alkoxide is reported.

(a) Copper(I) tert-Butoxide: Cu(OBu^t)

The preparation of copper(I) tert-butoxide involves the preparation of the lithium alkoxide, followed by its reaction with copper(I) chloride in a method analogous to that of the preparation of simple copper(II) alkoxides (see chapter 5):

$$Bu^tOH + BuLi \longrightarrow Li(OBu^t) + BuH$$

$$Li(OBu^t) + CuCl \longrightarrow Cu(OBu^t) + LiCl$$

In this case the product may be purified, yielding pale yellow crystals, either by re-crystallisation from hexane[71] or by sublimation[70]. Initial attempts to use the recrystallisation method failed as the hexane used, although dried with sodium wire, led to hydrolysis and disproportionation of the product. The sublimation method proved to be more successful with a yield of 72% being obtained.

Butyllithium was used instead of lithium metal to prepare the lithium alkoxide as it reacts more rapidly with tert-butanol. However it was essential that pure butyllithium was used as otherwise a hydrocarbon oil was formed together with an unidentified yellow solid (not copper(I) tert-butoxide).

The copper(I) tert-butoxide was highly air- and moisture-sensitive, so great care had to be taken when preparing and storing it. The mass spectrum and infra red spectrum were both in good agreement with the literature[70,71]. However the elemental analysis was quite poor with the copper analysing lower than required and carbon and hydrogen analysing higher than expected. The low copper analysis may be due to hydrolysis of the product either prior to or during analysis but the high carbon analysis cannot be explained in this way so it would appear that the product is not quite pure, there being some hydrocarbon contamination. The copper(I) tert-butoxide was, however, used without further purification, as the presence of a small quantity of hydrocarbon would not affect its reactivity. It should, if required, be possible to prepare an analytical sample by re-crystallisation from hexane dried by refluxing with sodium with benzophenone as indicator. However this was not considered to be necessary for the present study.

The reactions described above involved the use of two reaction vessels: in one lithium tert-butoxide was prepared by adding butyllithium to tert-butanol in THF and the resulting solution was then added to a slurry of copper(I) chloride in THF in the second vessel. An attempt was made to carry out a "one pot" reaction where butyllithium was added to a mixture of copper(I) chloride and tert-butanol in THF. However this led to the formation of a black solution with a coppery precipitate, presumably due to the disproportionation of a copper(I) species. This may be the copper(I) chloride or may be the product of the reaction of the lithium alkyl with copper(I) chloride. Therefore it would appear that it is necessary to carry out the preparation in the two stages described above.

(b) Copper(II) 2-(2-Methoxyethoxy)ethoxide: $Cu(OCH_2CH_2OCH_2CH_2OCH_3)_2$

The preparation of copper(II) 2-(2-methoxyethoxy)ethoxide made use of the alcohol exchange reaction between copper(II) methoxide and

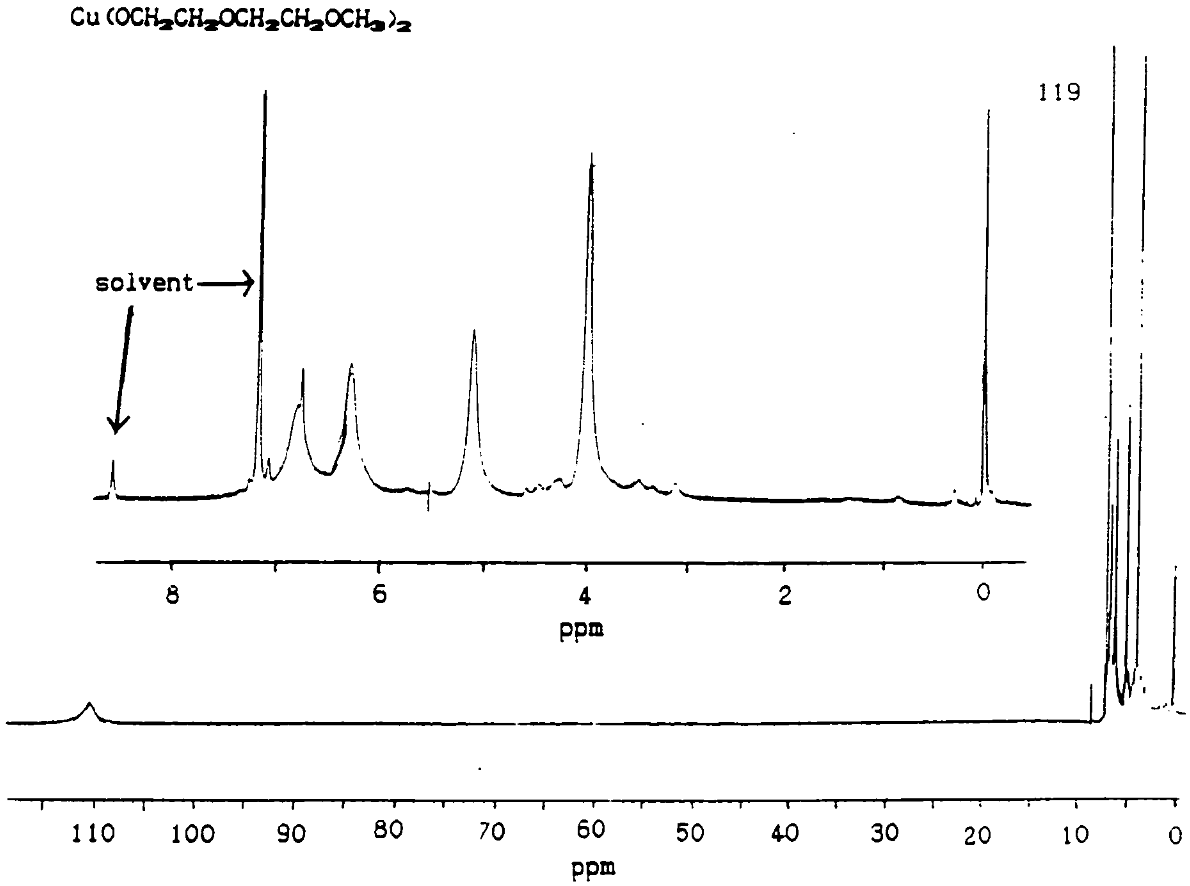
2-(2-methoxyethoxy)ethanol[158]:

$Cu(OMe)_2 + 2CH_3OCH_2CH_2OCH_2CH_2OH \rightarrow Cu(OCH_2CH_2OCH_2CH_2OCH_3)_2 + 2CH_3OH$

The literature method involved precipitating the alkoxide from benzene, using hexane, having already pushed the alcohol exchange to completion by removing methanol from the system as its benzene azeotrope. Initially toluene was used as the solvent, for the obvious safety reasons, but this led to the formation of a glutinous mass which could not be filtered to remove any unreacted methoxide. Thus a second reaction was carried out, this time using benzene as solvent, but this led to the same problem as above. The addition of hexane in an attempt to precipitate the product had no effect on the viscosity of the mixture. However, the addition of a small quantity of pyridine to the glutinious mass led to the immediate formation of a mobile solution which was readily filtered, the product being collected in a 49% yield by evaporating the solution to dryness. A better yield (71%) was achieved by using a benzene/pyridine mixture as solvent during the alcohol exchange, rather than adding the pyridine after the exchange.

The difficulties encountered during the above preparation were probably due to the degree of oligomerisation of the product, a factor likely to affect its solubility and viscosity. The presence of ether oxygens in the ligand are thought to reduce the extent of alkoxide bridging, and thus the degree of oligomerisation, when compared to that in simple alkoxides due to the oxygens' chelating to copper[158]. This view is inspite of the evidence of the ^1H NMR of the alkoxide in deutero benzene/pyridine which shows one resonance highly shifted and broadened by the paramagnetic Cu^{2+} at δ 110.6ppm with the other four resonances being only slightly shifted at δ 6.75-4.00ppm indicating that the ligand does not chelate to the copper (see Figure 7.1). It is, however, possible that if a small number of ligands chelate, thus limiting the size of the oligomers, then the ^{1}H NMR resonances of this small proportion of ligands would be broadened to invisibility. It is likely that the addition of pyridine forms a mobile solution as it leads to the formation of smaller oligomers due to the pyridine coordinating to copper thus preventing ligands bridging to such a large degree.

A discrepancy was observed between the literature[158] value for the metal-oxygen stretch in copper(II) 2-(2-methoxyethoxy)ethoxide of 455cm^{-1} and the observed value of 490cm^{-1}. On exposure of the mull to air the alkoxide was rapidly hydrolysed and the metal oxygen stretch was shifted to 465cm^{-1} which is nearer to the literature value which may explain the original discrepancy.



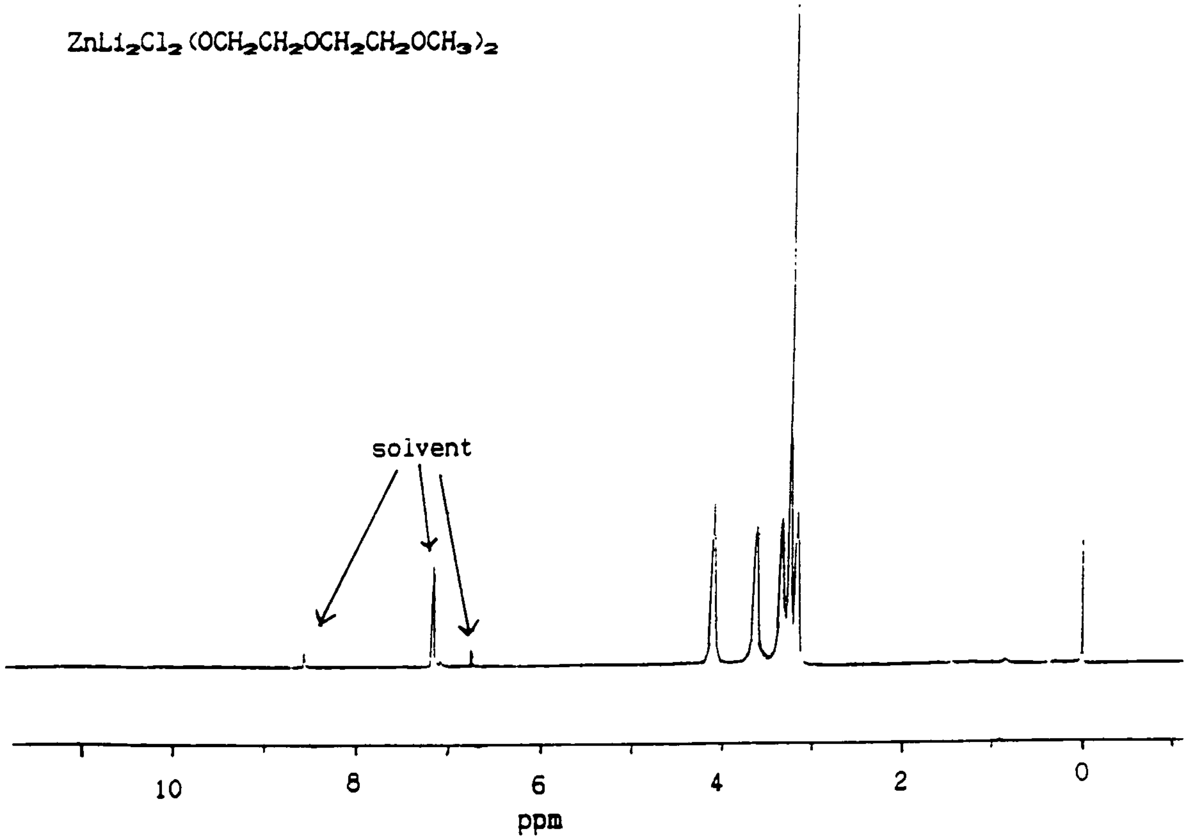


Figure 7.1: ^{1}H NMR Spectra of Cu(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$ and ZnLi$_2$Cl$_2$(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$ in C_6D_6/C_5D_5N

(c) Zinc 2-(2-Methoxyethoxy)ethoxide: $Zn(OCH_2CH_2OCH_2CH_2OCH_3)_2$

The attempted preparation of zinc 2-(2-methoxyethoxy)ethoxide by the reaction of zinc chloride with lithium 2-(2-methoxyethoxy) ethoxide led to the formation of a compound which analysed as $Li_2ZnCl_2(OCH_2CH_2OCH_2CH_2OCH_3)_2$ in a 72% yield:

$$CH_3OCH_2CH_2OCH_2CH_2OH + BuLi \longrightarrow Li(OCH_2CH_2OCH_2CH_2OCH_3) + BuH$$

$$ZnCl_2 + 2Li(OCH_2CH_2OCH_2CH_2OCH_3) \longrightarrow Li_2ZnCl_2(OCH_2CH_2OCH_2CH_2OCH_3)_2$$

This new compound was found to be insoluble in benzene and THF but soluble in pyridine or benzene/pyridine mixtures. The spectral evidence discussed below does not indicate whether any Zn-Cl bonds were actually broken in the reaction. In other words, the product may be a zincate type species: $Zn(OR)_2(Cl)_2^{2-}$ with two Li^+ as counter ions or a lithium chloride adduct of the desired alkoxide. A structural investigation of this compound would therefore be very interesting to establish the position of the lithium and chlorine atoms and also to determine whether the ligand chelates. Attempts to grow suitable crystals were, however, unsuccessful.

The infra red spectrum was similar to that of copper(II) 2-(2-methoxyethoxy)ethoxide with the metal-oxygen stretch being at $505cm^{-1}$. The ^7Li NMR spectrum showed only one resonance indicating that the two lithium atoms are equivalent, whilst the ^1H NMR showed five slightly shifted resonances at δ 4.12-3.17ppm. It is interesting to note that unlike copper(II) 2-(2-methoxyethoxy)ethoxide the methyl protons are not the least deshielded, instead a set of methylene protons are (see Figure 7.1). This suggests that the oxygen nearest the methyl group chelates to the zinc or has a lithium coordinated to it thus deshielding the protons on the adjacent carbons.

Whilst the above compound is very interesting from a structural point of view, it would be more advantageous, as far as the project as a whole is concerned, if the alkoxide could be made without the lithium and chlorine being present due to the poisoning effect of chloride in copper based catalysts. It was for this reason that the reaction between the alcohol and diethylzinc was carried out in an analogous way to the preparation of zinc methoxide in chapter 5. The addition of diethylzinc to the alcohol led to some fuming but no other sign of reaction. Warming to 60°C caused the reaction mixture to set, so pyridine was added forming a clear gold-coloured solution. An oily substance was formed on removing solvent under reduced pressure which may in fact have been the desired alkoxide. A work-up was attempted by extraction using THF followed by precipitation with hexane, but proved unsuccessful as the oily substance was only slightly soluble in THF and the small quantity of precipitate formed on the addition of hexane rapidly redissolved. The alcohol exchange reaction between zinc methoxide and 2-(2-methoxyethoxy)ethanol, whilst not yet investigated, would be expected to give the zinc alkoxide.

7.2.2 Preparation of Hydroxycarboxylates

The preparation of zinc hydroxycarboxylates involved the reaction of solutions of zinc nitrate and solutions of the sodium salts of the hydroxycarboxylic acids concerned. The pH of the reaction mixture was crucially important as basic salts were produced if the pH was too high and free acid impurities were present if the pH was too low. An example of this is recorded in the experimental section (7.3.2 b) where an attempted preparation of zinc 4-hydroxybenzoate resulted in a product contaminated with 4-hydroxybenzoic acid.

(a) Zinc 2-Hydroxybenzoate: $Zn(O_2CC_6H_4(OH))_2$

Zinc 2-hydroxybenzoate was prepared as a dihydrate by adding a solution of sodium 2-hydroxybenzoate to a solution of zinc nitrate at pH 4.4-4.7:

$$Zn(NO_3)_2 + 2Na(O_2CC_6H_4(OH)) \longrightarrow Zn(O_2CC_6H_4(OH))_2 + 2NaNO_3$$

A crystal structure[118] of this compound shows that the zinc is surrounded by four oxygens, two from water of crystallisation and two from carboxylate groups, in a tetrahedral geometry (see Figure 7.2). The hydroxy group is not involved in bonding to the zinc and so should be open to attack by the soluble copper alkoxides discussed above.

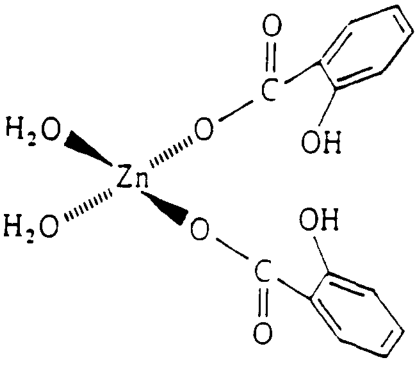


Figure 7.2: Crystal Structure of Zinc 2-Hydroxybenzoate Dihydrate[118]

Zinc 2-hydroxybenzoate dihydrate was readily dehydrated by heating to 105°C for two hours under vacuum. The anhydrous material produced was insoluble in dry THF but was soluble in THF which had not been dried, whilst the hydrated material was soluble in dry THF. Therefore it appears that some water is necessary for zinc 2-hydroxybenzoate to be soluble in THF, but in order to investigate reactions of zinc 2-hydroxybenzoate with the soluble copper alkoxides, an anhydrous system is required. The addition of an excess of pyridine to a slurry of zinc 2-hydroxybenzoate in dry THF led to dissolution, but after a few seconds a precipitate was formed. This is in contrast to when an equimolar amount of pyridine was added to a slurry of zinc 2-hydroxybenzoate in dry THF which led to complete and lasting dissolution. These observations suggest that a mono-pyridine complex is formed which is soluble in THF, but that any excess pyridine leads to the formation of insoluble "poly-pyridine" complexes.

(b) Zinc Tartrate: $Zn(O_2CCH(OH)CH(OH)CO_2)$

Zinc tartrate was prepared as a dihydrate by adding a solution of sodium tartrate to a solution of zinc nitrate at pH 3.0-3.5:

$$Zn(NO_3)_2 + Na_2(O_2CCH(OH)CH(OH)CO_2) \rightarrow Zn(O_2CCH(OH)CH(OH)CO_2) + 2NaNO_3$$

Zinc tartrate dihydrate was readily dehydrated by heating to 110°C for two hours. The anhydrous material was found to be insoluble in organic solvents, indeed it is insoluble in water. This fact was disappointing as the hydroxycarboxylates are more likely to react with the soluble copper alkoxides if they are in solution.

7.2.3 Reactions of Copper(I) tert-Butoxide and Zinc 2-Hydroxybenzoate

The reaction between copper(I) tert-butoxide and zinc 2-hydroxybenzoate was more complex than had been expected, indeed, sometimes several different products precipitated successively from one reaction. The reactions all involved adding a solution of copper(I) tert-butoxide to a THF/pyridine solution of zinc 2-hydroxybenzoate with varying stoichiometries. The products, which separated immediately or on concentrating and cooling the solutions, had similar infra red spectra which all showed the loss of the OH stretch at 3205cm^{-1} when compared to the spectrum of anhydrous zinc 2-hydroxybenzoate. Most of the analyses of the products could be fitted to a molecular formula, indicating the presence of either a pure compound or a stoichiometric mixture of compounds. However the stoichiometry of the reactants was not necessarily reflected in the products, indeed some of the products appeared to have copper in varying oxidation states. The products have been assigned to groups depending on their stoichiometry: Type I, $Cu_3Zn_2(oHB)_4Py_n$ or $Cu_2Zn_3(oHB)_4Py_n$; Type II, $Cu_2Zn_2(oHB)_3Py_n$; Type III, $Cu_4Zn(oHB)_2(O)Py_n$; Type IV, $Zn(oHB)Py_n$ where (oHB) represents $(O_2CC_6H_4O)$. A summary of the reactions and their products is given in Table 7.1.

Table 7.1 Summary of Reactions of Copper(I) tert-Butoxide and Zinc 2-Hydroxybenzoate

Moles of			Product	Yield	Product Type
Cu(OBu^t)	Zn(sal)$_2$	Py			
2	1	4	$Cu_3Zn_2(oHB)_4Py_4$	^{1}43%	I
			$Cu_2Zn_2(oHB)_3Py_3$	^{1}4%	II
			$Cu_3Zn_2(oHB)_4Py_3$	^{1}22%	I
1	1	1	$Zn(oHB)Py_{0.4}$	^{1}11%	IV
			$Cu_2Zn_3(oHB)_4Py_3$	^{1}12%	I
2	1	1	$Cu_4Zn(oHB)_2OPy_{1.4}$	^{2}51%	III
			$Cu_2Zn_2(oHB)_3Py_2$	^{2}8%	II
2	1	1	$Cu_3Zn_2(oHB)_4Py_2$	^{1}87%	I
4	1	1	$Cu_4Zn(oHB)_2OPy_{1.2}$	^{2}79%	III

Notes:

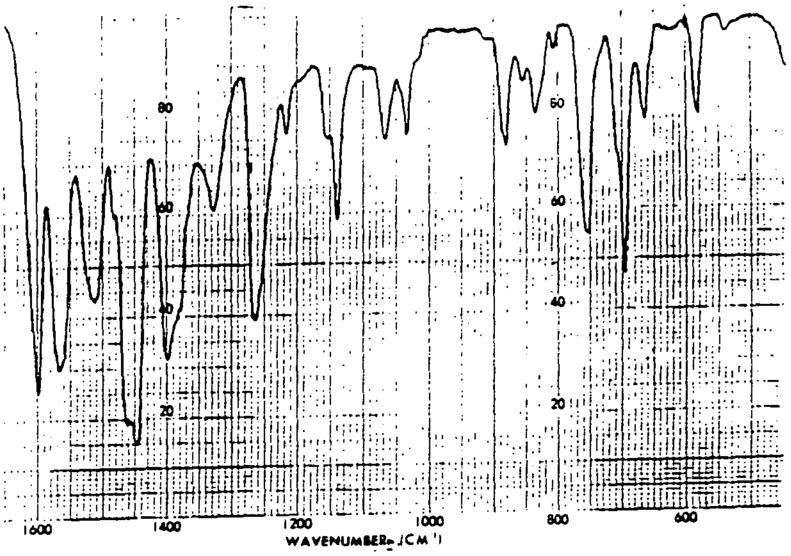
1. Yield based on Zinc.
2. Yield based on Copper.
3. (sal) represents $(O_2CC_6H_4(OH))$.
4. (oHB) represents $(O_2CC_6H_4O)$.

The discussion that follows starts by considering the infra red spectra of the products and then goes on to consider the oxidation state of copper in products of Type I stoichiometry. The final two sections are concerned with the extraction of some of the products with pyridine and their impregnation on to alumina extrudate.

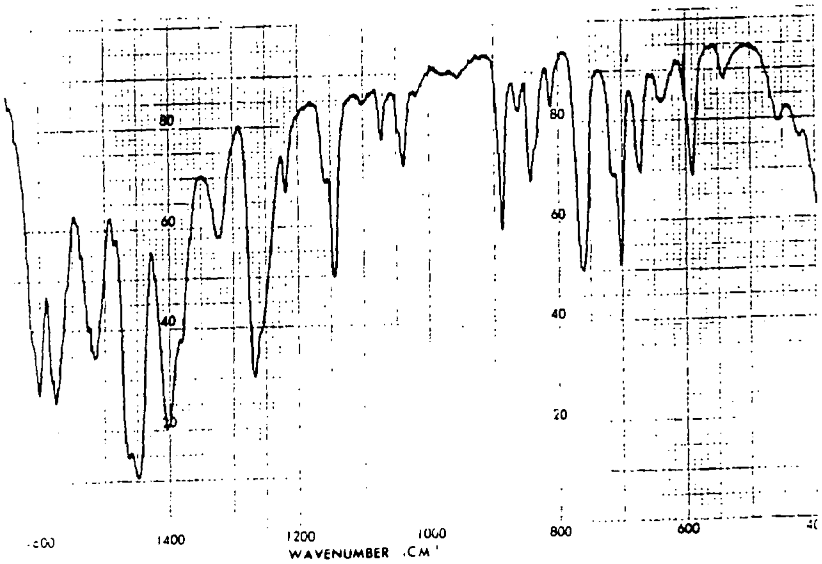
(a) Infra Red Spectra

As previously stated the infra red spectra of all the species are very similar which is to be expected as they all contain the

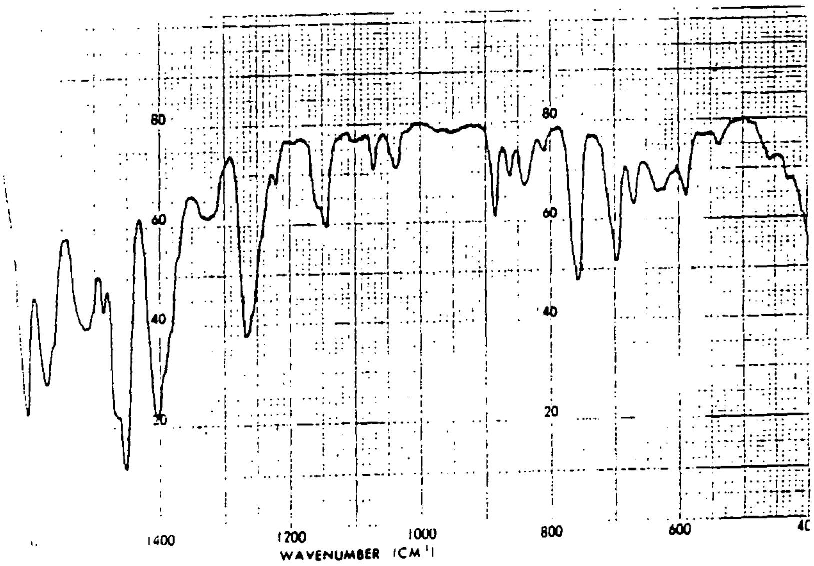
$(O_2CC_6H_4O)^{2-}$ residue. The spectra of compounds of the same type were identical and, indeed the spectra of compounds of types I, II and III were almost identical with some changes in the relative intensities of some absorptions being the only differences (see Fig 7.3). The spectrum of the type IV compound was slightly different to the other types with some absorptions shifted (cm^{-1}): 1240, shifted from 1265 (C-O stretch); 820, shifted from 840; 770/750 doublet instead of a singlet at 760 (H out of plane for 1,2-disubstituted aromatic). These differences can be explained as in this compound the metal appears to be coordinated to both the alkoxy and carboxylato oxygens of one ligand whereas in the other cases bridging occurs (see Fig 7.4). The spectra of compounds of types I-IV are all different to that of anhydrous zinc 2-hydroxybenzoate in several ways: generally the absorptions are all sharper; total loss of the OH stretch at $3205cm^{-1}$; between $1650-1500cm^{-1}$ there are major changes (carbonyl region); between $1350-1200cm^{-1}$ there are major differences (C-O region); changes in relative intensities of several absorptions (see Fig 7.4). The changes in the hydroxy, carbonyl and C-O regions are only to be expected for the reactions which have occurred.



Type I: $Zn_2Cu_3(oHB)_4Py_4$

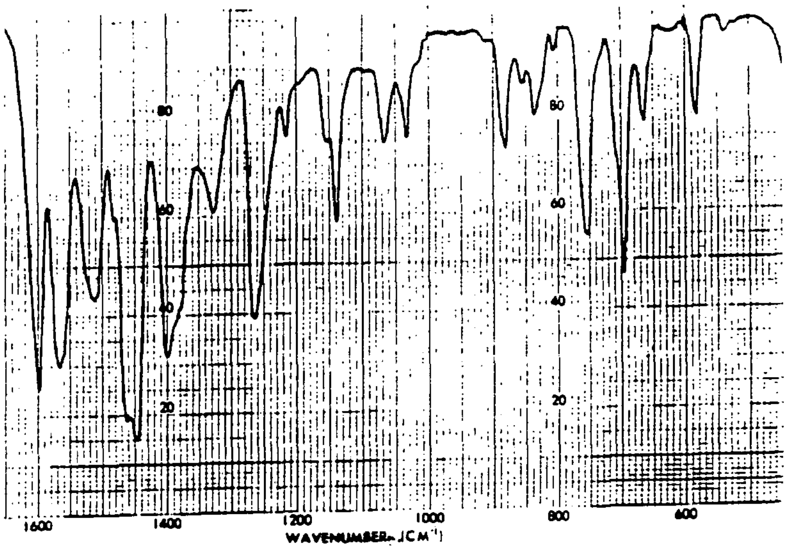


Type II: $Cu_2Zn_2(oHB)_3Py_2$

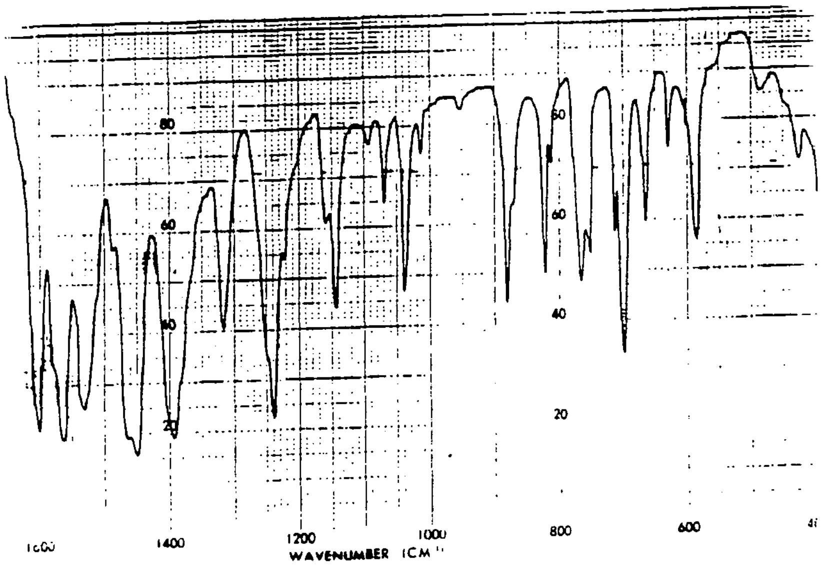


Type III: $Cu_4Zn(oHB)_2OPy_{1.4}$

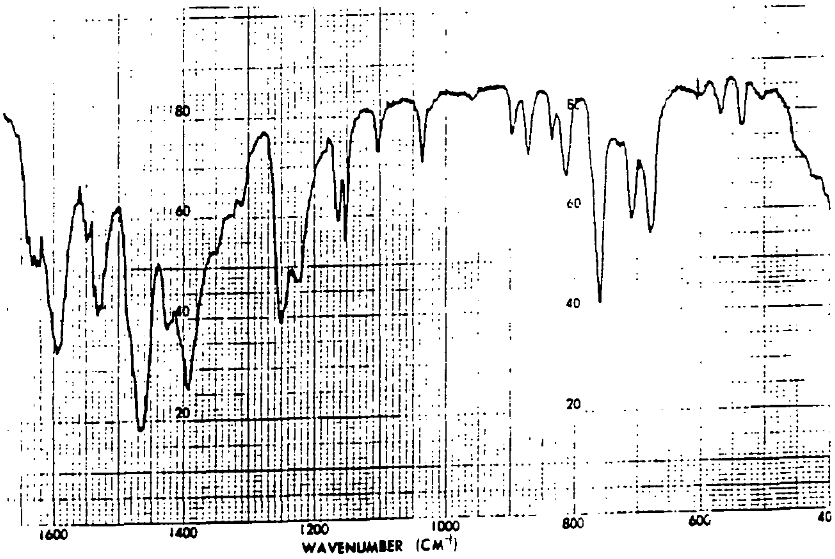
Figure 7.3: Infra Red Spectra of Product Types I, II and III



Type I: $Zn_2Cu_3(oHB)_4Py_4$



Type IV: $Zn(oHB)Py_{0.4}$



Anhydrous Zinc 2-Hydroxybenzoate

Figure 7.4: Infra Red Spectra of Product Types I and IV and Anhydrous Zinc 2-Hydroxybenzoate

(b) Oxidation State of Copper in Type I Products

Products of Type I stoichiometry in Table 7.1 (e.g. $Cu_3Zn_2(oHB)_4Py_2$ appear to contain copper in different oxidation states. This statement assumes that all of the hydroxy protons had been removed from the hydroxybenzoate group as indicated by the infra red spectra which showed no evidence for an OH stretch. In addition to the usual nujol mull, a spectrum was recorded using a perfluorokerosene mull to ensure that the C-H stretches of nujol had not masked an O-H stretch.

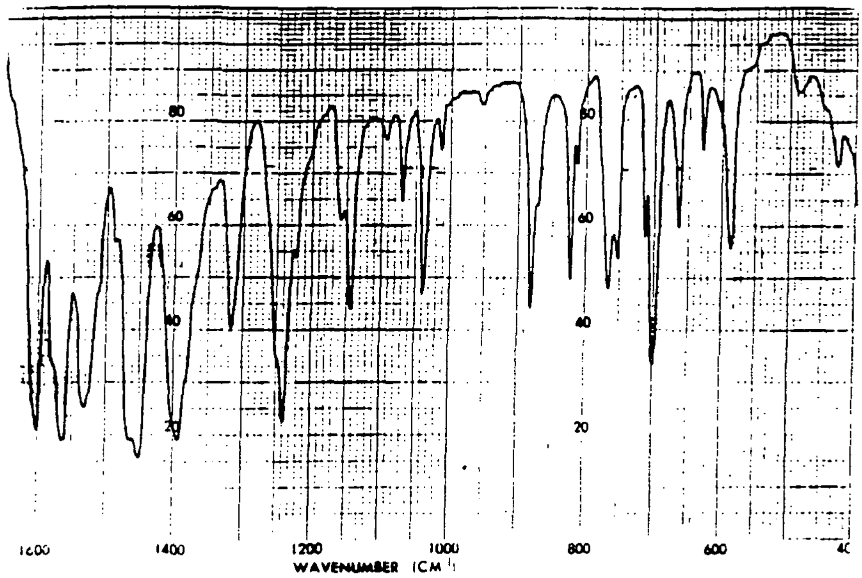
For any copper to be present in the +2 oxidation state, a species in the system would have had to have been reduced. The disproportionation of copper or the evolution of hydrogen are possibilities, but no conclusive evidence for either was observed. The substance dissolved completely in a large excess of pyridine (10ml pyridine, 0.066g solid) so copper metal was not formed. It is more likely that the substance contains one copper in the +2 oxidation state and two in the +1 state (i.e. one paramagnetic copper) rather than two in the +2 state and one in the zero state (i.e. three paramagnetic coppers) as very few copper(0) complexes have been observed[159]. The magnetic moment of $Cu_3Zn_2(oHB)_4Py_2$ (μ_{eff} = 1.18BM) tends to support this contention, although the accuracy of this value is not certain due to the size of the estimated diamagnetic correction[160] compared to the size of the measured magnetic moment.

(c) Extraction of Product Types I and IV with Pyridine

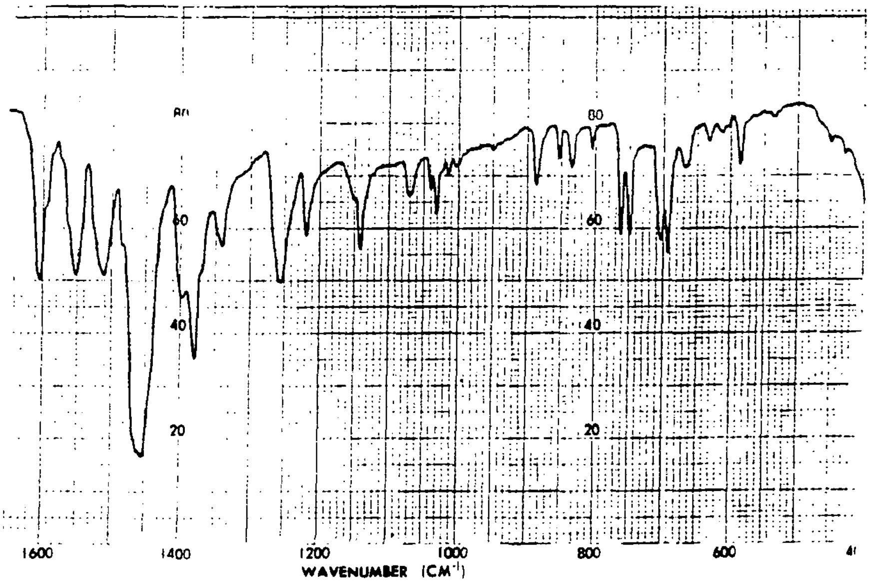
On investigating the solubility of the final two compounds in

Table 7.1, in order to carry out exploratory impregnation studies, three further products were isolated. The substances were insoluble in ether solvents, such as THF, monoglyme and diglyme but were soluble in pyridine.

When $Cu_4Zn(oHB)_2OPy_{1.2}$ was extracted with pyridine, a clear dark green solution was obtained together with a small quantity of pale brown solid. A large number of tiny green needles separated from this solution. The infra red spectrum of these crystals showed no absorption due to any OH stretch and they analysed as $Cu(oHB)Py_2$ indicating that the copper is in the +2 oxidation state. It is apparent that the original compound had undergone disproportionation and that the undissolved material was likely to be copper metal. A crystal structure of this compound, which can be assigned to product Type IV above, is underway. The infra red spectrum of this compound was slightly different to that of $Zn(oHB)Py_{0.4}$ (Type IV from above) with some absorptions shifted (cm^{-1}): 1510 shifted from 1530; 1340 shifted from 1320; 1255 shifted from 1240; absorptions at 855 and 835 instead of one at 820 (see Fig 7.5). These changes can be accounted for by the change in metal.



Type IV: $Zn(oHB)Py_{0.4}$

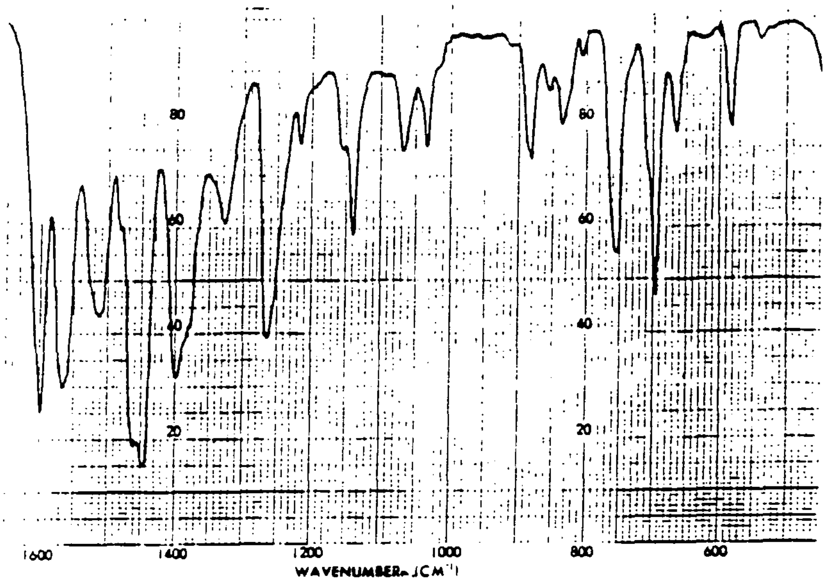


$Cu(oHB)Py_2$

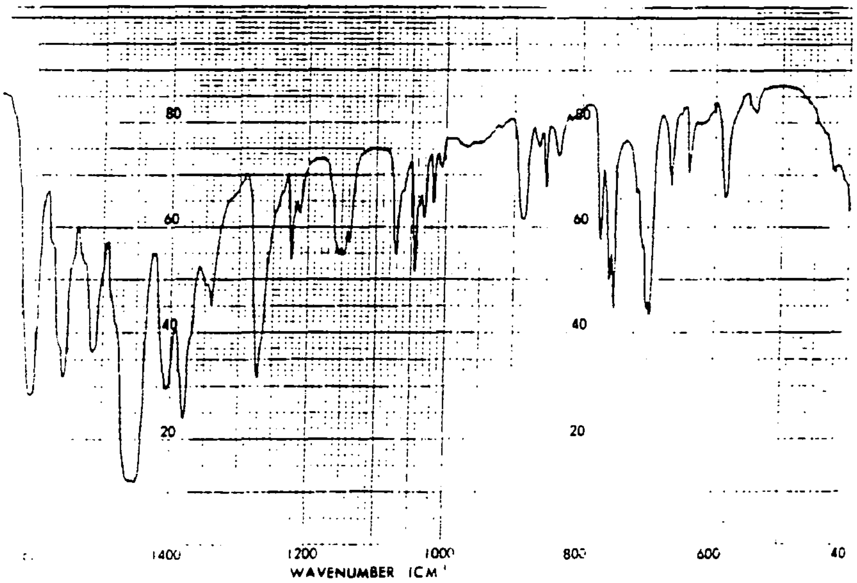
Figure 7.5: Infra Red Spectra of Product Type IV and $Cu(oHB)Py_2$

When $Cu_3Zn_2(oHB)_4Py_2$ was extracted with pyridine, a clear dark green solution was obtained together with some dark green solid. It is interesting that not all the solid dissolved in this case, whereas in a previous experiment (see above) it had all dissolved. Although this system was more concentrated (10ml pyridine, 1.01g solid) than before (10ml pyridine, 0.066g solid) the undissolved solid was different to the initial solid, analysing as $Cu_4Zn_5(oHB)_5O_2Py_{10}$. This analysis indicates an explanation for the above observation: the source of the oxygen, required to balance charges, was probably water, present in the pyridine and thus the compound was partially hydrolysed on mixing with the pyridine. The infra red spectrum of this product is very similar to that of Type I above save for some extra absorptions at (cm^{-1}): 1230, 1150, 1000-1050, 700-800 (see Fig 7.6).

A large number of tiny green crystals separated from the dark green solution which analysed best for $Cu_3Zn(oHB)_3Py_6$. However there was evidence of inhomogeneity: green needles and a much paler green powder was observed under a microscope (x60). The infra red spectrum of the product was identical to that of $Cu(oHB)Py_2$ (see Fig 7.7) and more importantly a Weissenberg x-ray photograph of one of the crystals was identical to such a photograph of a crystal of $Cu(oHB)Py_2$. It is therefore reasonable to regard the product as a mixture of $Cu(oHB)Py_2$ and ZnO which still sataisfies the elemental analysis reasonably well, despite the presence of an extra oxygen atom.

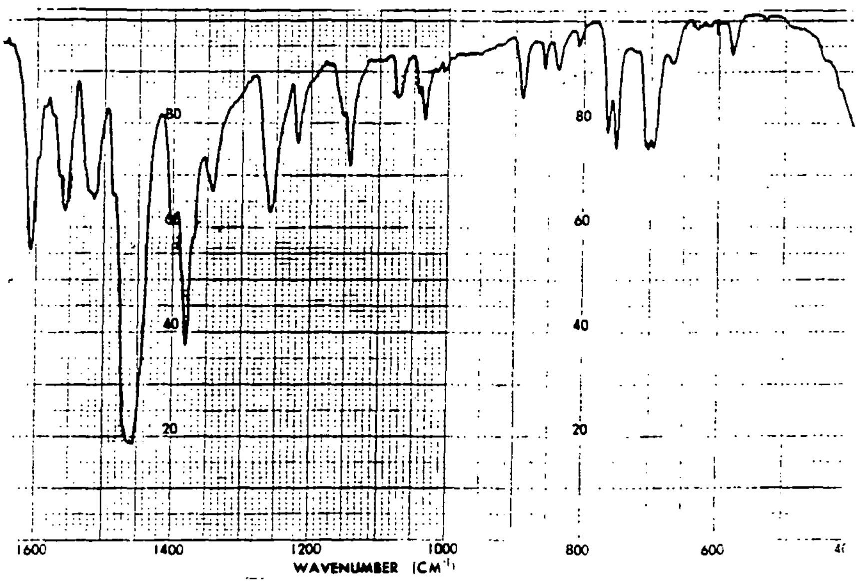


Type I: $Zn_2Cu_3(oHB)_4Py_4$

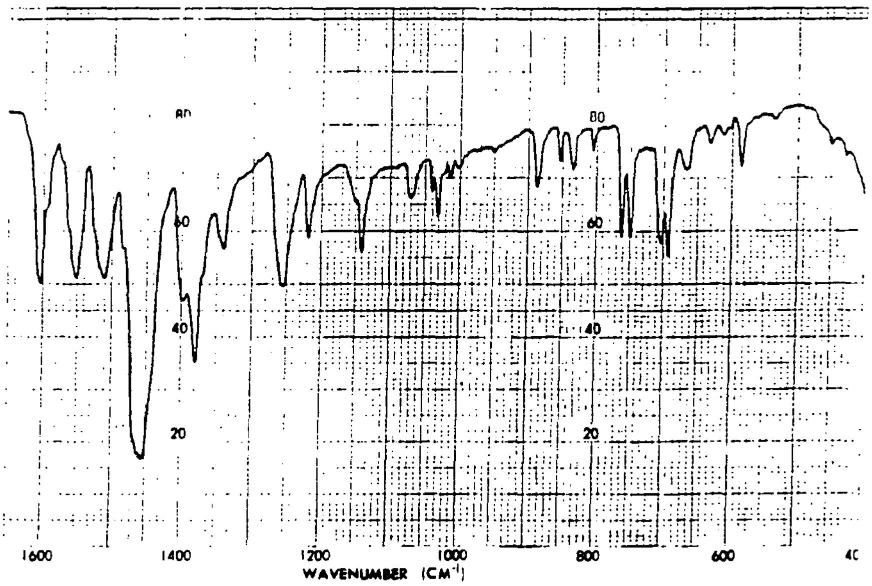


$Cu_4Zn_5(oHB)_5O_2Py_{10}$

Figure 7.6: Infra Red Spectra of Product Type I and $Cu_4Zn_5(oHB)_5O_2Py_{10}$



Cu(oHB)Py$_2$/ZnO



Cu(oHB)Py$_2$

Figure 7.7: Infra Red Spectra of Cu(oHB)Py$_2$/ZnO and Cu(oHB)Py$_2$

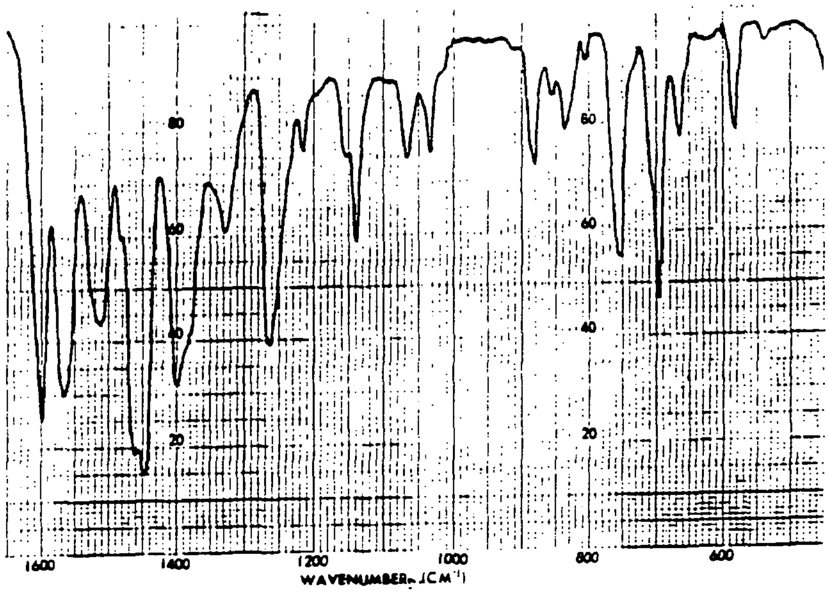
(d) Impregnation of Product Types I and IV on to Alumina Extrudate

As previously stated, the investigation of solubilities dicussed above was carried out during exploratory studies into the impregnation of the compounds on to an alumina extrudate (supplied by ICI). The two impregnations resulted in materials with disappointingly low copper loadings of only 2%, whose thermal decomposition resulted in the evolution of carbon dioxide and pyridine and the formation of purple/red coloured materials which were both tested at ICI Billingham. The material formed using $Cu_4Zn(oHB)_2OPy_2$ had an immeasurably small copper surface area as measured by nitrous oxide titration whilst the material formed using $Cu_3Zn_2(oHB)_4Py_2$ had negligible methanol synthesis activity in a microreactor test. These poor results were probably due to the very low copper loading, so more work is necessary to try and increase this loading.

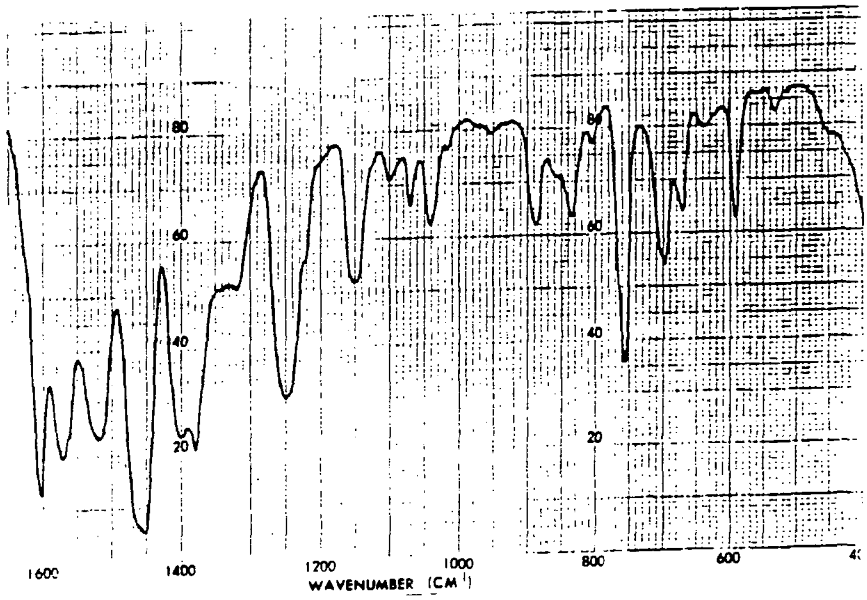
7.2.4 Reactions of Copper(II) 2-(2-methoxyethoxy)ethoxide and Zinc Hydroxycarboxylates

(a) The reaction between copper(II) 2-(2-methoxyethoxy)ethoxide and anhydrous zinc 2-hydroxybenzoate in THF and pyridine (ratio, Cu:Zn:Py, 1:1:1) resulted in the formation of a product which appeared to consist mainly of $CuZn(oHB)_2Py$ contaminated with a small quantity of Zn(oHB) in an approximately 50% yield. The infra red spectrum of this material is almost identical to Types I-III above with some subtle differences in the absorptions (cm^{-1}): 1250 shifted from 1260; different shape to absorption at 1150; new absorption at 1100 (see

Fig 7.8). The solubility and thus impregnation of this material on to an alumina extrudate was not investigated.



Type I: $Zn_2Cu_3(oHB)_4Py_4$



$CuZn(oHB)_2Py/Zn(oHB)$

Figure 7.8: Infra Red Spectra of Product Type I and

$CuZn(oHB)_2Py/Zn(oHB)$

(b) The effect of adding a solution of copper(II) 2-(2-methoxyethoxy)ethoxide to a slurry of anhydrous zinc tartrate was investigated in case any reaction occurred despite the insolubility of the zinc tartrate. Unfortunately the solid recovered after several hours of mixing consisted of anhydrous zinc tartrate (ir) with a slight impurity of copper (elemental analysis Zn:Cu, 38:1).

7.2.5 Summary

The work discussed in this chapter has resulted in the formation of, apparently, mixed metal compounds of copper and zinc which was one of the primary goals of this project. There is great potential for making copper-zinc compounds using this method or variations based on it as, in principle, the stoichiometry and spacing of the copper and zinc atoms in such compounds may be varied by utilising different hydroxycarboxylates. However, the particular system chosen for more detailed study: copper(I) tert-butoxide and anhydrous zinc 2-hydroxybenzoate, proved to be far more complex than expected and further study is required to explain more fully the observations made. The use of a soluble copper(II) alkoxide has also resulted in the formation of an apparently mixed metal compound, namely $CuZn(oHB)_2Py$, but again more study is required to confirm and exploit the observations made above.

The reactions described above involved the use of copper alkoxides and zinc hydroxycarboxylates but the reverse, i.e. zinc alkoxides and copper hydroxycarboxylates, would be equally valid and may even prove to be more useful. In the course of this study it was shown that soluble zinc alkoxides can be made, whilst the problems encountered with the low solubility of zinc hydroxycarboxylates may be overcome by using copper hydroxycarboxylates rather than zinc ones. This is because copper hydroxycarboxylates are more likely to be complexed and thus solubilised by nitrogen donor ligands, such as pyridine than their zinc counterparts due to copper's greater affinity for nitrogen donor ligands compared to zinc.

7.3 Experimental

7.3.1 Preparations of Alkoxides

(a) Preparation of Copper(I) tert-Butoxide: Cu(OBu^t)

(i) To a solution of tert-butanol (9ml, 0.095mol) in dry THF (30ml) at -10°C was added slowly, with caution, a solution of butyllithium (freshly supplied) in hexane (40ml, 1.59M, 0.063mol). The resulting, clear, solution was added to a slurry of purified[161] copper(I) chloride (6.1681g, 0.0623mol) in dry THF (20ml) producing a yellow/brown solution. Solvent was removed under reduced pressure and the resulting yellow powder was dried in vacuo. A cold finger was inserted into the reaction vessel and the temperature of the system raised. At 100°C (oil bath temperature) the powder turned purple in colour and a small amount of an off white sublimate was observed. After cleaning the cold finger the temperature was raised to 175°C and a yellow sublimate was formed on the cold finger. Heating continued for 3 hours after which time 2.45g of product was collected. A further quantity (3.65g) of sublimate was collected by heating the sublimator to 180°C for 4 hours. The yellow sublimate turned a little brown on handling in the Faircrest glove box. Yield 6.10g (72%). The product was characterised as follows:

Analysis	Found:	C,36.9; H,6.9; Cu,41.1 %
	C_4H_9CuO Req:	C,35.1; H,6.6; Cu,46.5 %

Infra Red (Nujol, cm^{-1}): 3000-2800, 1460, 1380(nujol); 1360(s); 1240; 1185(s); 1025; 965(sh); 940(s); 765; 620; 550; 520; 490; 470.

Mass Spectrum: As per literature[158]: main peaks observed were:

m/e 544 Molecular ion.
m/e 529 corresponding to loss of CH_3 from molecular ion.
m/e 471 corresponding to loss of $(CH_3)_2CO$ from m/e 529.
m/e 414 corresponding to loss of $C(CH_3)_3$ from m/e 471
m/e 59 Base peak: fragment $(CH_3)_2CHO$
m/e 31 Fragment CH_3O.

(ii) To a mixture of copper(I) chloride (1.500g, 0.0151mol) and tert-butanol (2.0ml, 0.021mol) in dry THF (30ml) was added, slowly with caution, butyllithium in hexane (10ml, 1.59M, 0.016mol). The solution turned black with a copper-like colouration. Nothing further was done with this reaction.

(b) Preparation of Copper(II) 2-(2-methoxyethoxy)ethoxide:

$Cu(OCH_2CH_2OCH_2CH_2OCH_3)_2$

(i) To a slurry of copper(II) methoxide (1.583g, 0.0126mol) in dry toluene (100ml) was added 2-(2-methoxyethoxy)ethanol (10ml, 0.0841mol). The resulting mixture was heated to reflux temperature (oil bath at 120°C) and the methanol/toluene azeotrope was removed (temperature at top of column 65°C) leaving a dark blue viscous solution. Attempts to filter this failed as, on cooling, the solution became even more viscous. This preparation was therefore abandoned.

(ii) To a slurry of copper(II) methoxide (1.050g, 8.36mmol) in dry benzene (100ml) was added 2-(2-methoxyethoxy)ethanol (5ml, 0.0420mol). The resulting mixture was heated to reflux temperature (oil bath at 120°C) and the methanol/benzene azeotrope was removed (temperature at top of column 60°C) leaving a dark blue viscous solution, which on cooling became even more viscous, eventually turning jelly like. Hexane (30ml) was added in an attempt to precipitate the product, but no change was apparent, even on warming. Pyridine (5.0ml, 0.062mol) was added which led to the formation of a mobile solution which was filtered (No 3 stick) to remove the small quantity of insoluble material still present. Solvent was removed under reduced pressure yielding a blue solid which was dried in vacuo for several hours. Yield 1.24% (49%). The product was characterised as follows:

<u>Analysis</u> Found: C,38.1; H,7.3; Cu,21.6; N,0.0 %

$C_{10}H_{22}CuO_6$ Req: C,39.8; H,7.3; Cu,21.1 %

<u>Infra Red</u> (Nujol, cm^{-1}): 3000-2800(nujol); 2710(sh); 1600(w); 1460, 1380(nujol); 1370(sh); 1350(sh); 1300(sh); 1260; 1200; 1120(s); 1065(s); 1020(sh); 960(w); 920; 870; 840; 800; 720; 490(s); 420.

(iii) To a slurry of copper(II) methoxide (2.040g, 0.0162mol) in dry benzene (100ml) and pyridine (10ml, 0.124mol) was added 2-(2-methoxyethoxy)ethanol (10ml, 0.0841mol). The resulting mixture was heated to reflux temperature (oil bath at 100°C) and the methanol/benzene azeotrope was removed (temperature at top of column 60°C) leaving a dark blue solution. The solution was filtered (No. 3 stick) to remove any remaining copper(II) methoxide and the solvent was removed from the resulting clear blue solution under reduced pressure, yielding a blue powder which was dried in vacuo for several hours. Yield 3.50g (71%). The product was characterised as follows:

Analysis Found: C,38.8; H,7.4; Cu,21.3; N,0.0 %

$C_{10}H_{22}CuO_6$ Req: C,39.8; H,7.3; Cu,21.1 %

Infra Red (Nujol, cm^{-1}): 3000-2800(nujol); 2710(sh); 1460, 1380(nujol); 1370(sh); 1350(sh); 1300(sh); 1260; 1200; 1120(s); 1065(s); 1020(sh); 960; 920; 870; 840; 800; 720; 490(s); 420.

Melting Point 179-181°C (lit[7,12] 183-184)

^1H NMR (Solvent C_6D_6 with C_5D_5N, ppm): 110.6; 6.75, integral 2; 6.29, integral 2; 5.11, integral 2; 4.00, integral 3.

(c) Attempted Preparation of Zinc 2-(2-methoxyethoxy)ethoxide:

$Zn(OCH_2CH_2OCH_2CH_2OCH_3)_2$

(i) To a solution of 2-(2-methoxyethoxy)ethanol (6ml, 0.050mol) in dry THF at -10°C was added, slowly, with caution, butyllithium in hexane (25ml, 1.33M, 0.033mol). To the resulting, clear, colourless, solution was added a solution of anhydrous zinc chloride (2.28g, 0.017mol) in dry THF (10ml) which led to the formation of a white precipitate. The mixture was heated under reflux for 18 hours before filtering (No.3 stick). The white solid was washed with dry THF (3x30ml) and dried in vacuo. Yield 4.65g, (72%). The product was characterised as $Li_2ZnCl_2(OCH_2CH_2OCH_2CH_2OCH_3)_2$:

Analysis Found: C,30.9; H,5.8; Cl,18.2; Li,3.4; Zn,17.5 %

$C_{10}H_{22}Cl_2Li_2O_6Zn$ Req: C,30.9; H,5.7; Cl,18.3; Li,3.6; Zn,16.8 %

Infra Red (Nujol, cm^{-1}): 3000-2800(nujol); 2705(sh); 1460, 1380 (nujol); 1350; 1270; 1245; 1205; 1130(s, sh); 1095(s); 1070(sh); 1060(sh); 1020(s); 940(s); 890(s); 845; 830; 720(w); 580(s); 505(s); 455(w).

Melting Point 157-160°C

^{1}H NMR (Solvent C_6D_6 with C_5D_5N, ppm): 4.12, integral 2; 3.64,integral 2; 3.43, integral 2; 3.26, integral 3; 3.17, integral 2.

^{7}Li NMR (Solvent benzene with pyridine, ppm): 0.52.

(ii) To a solution of 2-(2-methoxyethoxy)ethanol (5ml, 0.042mol) in dry toluene (50ml) at -10°C, was added slowly, with caution, a solution of diethylzinc in toluene (15ml, 1.1M, 0.017mol) causing a slight fuming to occur. The mixture was allowed to warm to room temperature, with no apparent effect; on warming, the mixture "set" at 60-70°C (oil bath temperature). The addition of pyridine (5ml, 0.062mol) led to the formation of a clear, colourless solution which turned yellow/gold on heating to reflux. Removal of solvent under reduced pressure led to the formation of a gold coloured glutinous mass which was only slightly soluble in dry THF. Addition of dry hexane to this mixture led to the formation of a white precipitate which quickly redissolved. Addition of further hexane led to more precipitation but, again, the precipitate quickly redissolved. Cooling of the reaction mixture caused no change. No further work was carried out on this reaction.

7.3.2 Preparations of Hydroxycarboxylates

(a) Preparation and Dehydration of Zinc 2-Hydroxybenzoate Dihydrate: $Zn(O_2CC_6H_4(OH))_2.2H_2O$

To an aqueous solution of zinc nitrate (100ml, 1.00M) was added, dropwise, with vigorous stirring an aqueous solution of sodium 2-hydroxybenzoate (90ml, 2.00M) with the pH of the mixture being kept in the range 4.4-4.7 by means of the addition, when necessary, of dilute nitric acid (1M). A white precipitate was formed (first appeared after addition of 12ml sodium 2-hydroxybenzoate solution) which was separated by filtration, washed (water) and dried in air. Yield 22.5g (67%). The product was characterised as follows:

Analysis	Found:	C,44.9; H,3.6; Zn,17.6 %
	$C_{14}H_{14}O_8Zn$ Req:	C,44.8; H,3.8; Zn,17.4 % (dihydrate)

Infra Red (Nujol, cm^{-1}): 3700-2500(br,s); 3000-2800(nujol); 1620(sh); 1595(s); 1460, 1380(nujol); 1360; 1240; 1190(sh); 1150; 1095(w); 1035; 940(w); 870; 820; 760; 700; 670; 570; 530; 500(w); 410.

Zinc 2-hydroxybenzoate dihydrate (9.772g, 0.026mol) was dehydrated by heating to 105°C for 2 hours under vacuum. A mass loss of 0.98g was observed (theoretical loss 0.94g) and the moisture sensitive material so produced was characterised as follows:

Analysis Found: C,49.6; H,2.9; Zn,19.3 %

$C_{14}H_{10}06Zn$ Req: C,49.5; H,3.0; Zn,19.2 %

Infra Red (Nujol, cm^{-1}): 3205(br); 3000-2800(nujol); 1620(sh); 1595(s); 1550(sh); 1530; 1460(nujol); 1425(sh); 1380(nujol); 1350(sh); 1250(s); 1220(sh); 1160(sh); 1150; 1100(w); 1035; 900; 870; 835; 815; 760(s); 710; 680; 570; 535.

(b) Attempted Preparation of Zinc 4-Hydroxybenzoate:

$$Zn(O_2CC_6H_4(OH))_2$$

To an aqueous solution of zinc nitrate (30ml, 1.00M) was added, dropwise, with vigorous stirring an aqueous solution of sodium 4-hydroxybenzoate (40ml, 1.33M) with the pH of the mixture being kept in the range 4.3-4.6 by means of the addition, when necessary, of dilute nitric acid (1M). A white precipitate was formed which was separated by filtration, washed (water) and dried in air. Yield 5.3g. The product was characterised as follows:

Analysis Found: C,51.9; H,3.8; Zn,10.2; Na,0.8 %

$C_{14}H_{14}O_8Zn$ Req: C,44.8; H,3.8; Zn,17.4 % (dihydrate)

Infra Red (KBr disc, cm^{-1}): 3650- 2000(br); 1675(s); 1600(s); 1540; 1510; 1450(sh); 1400(br); 1320; 1290(sh); 1240(s); 1170(s); 1150(sh); 1130(w); 1100; 1010; 930; 880(w); 855(s); 790; 780; 770; 700; 640; 620; 550; 505; 430.

(c) Preparation and Dehydration of Zinc Tartrate Dihydrate:

$$Zn(O_2CCH(OH)CH(OH)CO_2).2H_2O$$

To an aqueous solution of zinc nitrate (40ml, 1.00M) was added, dropwise, with vigorous stirring an aqueous solution of sodium tartrate (20ml, 2.00M) with the pH of the mixture being kept in the range 3.0–3.5 by means of the addition, when necessary, of dilute nitric acid (1M). A white precipitate was formed which was separated by filtration, washed (water) and dried in air. Yield 7.94g (80%). The product was characterised as follows:

Analysis Found: C,18.8; H,3.4; Zn,26.5 %
$C_4H_8O_8Zn$ Req: C,19.3; H,3.2; Zn,26.2 % (dihydrate)

Infra Red (KBr disc, cm^{-1}): 3750–2500(br); 1600(br,s); 1420; 1380; 1330(w); 1310(w); 1290; 1240; 1110; 1090(sh); 1050; 1010(w); 930; 885; 740(sh); 715; 630; 540.

Zinc tartrate dihydrate (4.0223g, 0.016mol) was dehydrated by heating to 110°C for 2 hours under vacuum. A mass loss of 0.60g was observed (theoretical loss 0.58g) and the moisture sensitive material so produced was characterised as follows:

Analysis Found: C,21.9; H,1.9; Zn,30.9 %
$C_4H_4$06Zn Req: C,22.5; H,1.9; Zn,30.6 %

Infra Red (Nujol, cm^{-1}): 3405(br); 3000–2800(nujol); 1675(sh); 1590(br,s); 1460(nujol); 1420; 1380(nujol); 1310(w); 1270(w); 1250; 1090(s); 1050; 1015(w); 930(w); 885; 815; 740; 640; 560; 500(w).

7.3.3 Reactions of Copper(I) tert-Butoxide and Zinc 2-Hydroxybenzoate

Several reactions were carried out between copper(I) tert-butoxide and zinc 2-hydroxybenzoate using varying stoichiometries:

(a) To a slurry of zinc 2-hydroxybenzoate (2.493g, 7.36mmol) in THF (30ml) was added pyridine (2ml, 24.7mmol) which led to dissolution. After a few seconds a white solid reappeared so the mixture was filtered (No 4 stick) to give a clear colourless solution. To this was added a gold coloured solution of copper(I) tert-butoxide (2.012g, 14.7mmol) in THF (40ml) causing the solution to turn yellow with a green precipitate appearing after approximately half of the addition. The mixture was filtered (No 3 stick) to give a clear dark green solution and a dark green/purple coloured solid which was dried in vacuo. A further dark green solid was formed on cooling the solution to -20°C which was collected as above. On concentrating the residual solution under reduced pressure (25% solvent removed) and cooling to -20°C a third solid was produced which was collected as above. The solids were characterised as follows:

Solid 1: Yield 1.85g (43% if $Cu_3Zn_2(oHB)_4Py_4$, based on Zinc)

Analysis Found: C,48.6; H,3.5; Cu,16.1; N,4.4; Zn,11.8 %

$C_{48}H_{36}Cu_3N_4O_{12}Zn_2$ Req: C,48.8; H,3.1; Cu,16.1; N,4.7; Zn,11.1 %

Infra Red (Nujol, cm^{-1}): 3050(w,sh); 3000-2800(nujol); 1600(s); 1565(s); 1510; 1460(sh, nujol); 1445(s); 1400(s); 1380(sh, nujol); 1330; 1265(s); 1220; 1155(sh); 1140; 1070; 1035; 880; 855(w); 840; 810(w); 755(s); 695(s); 665; 580; 540(w).

Solid 2: Yield 0.12g (4% if $Cu_2Zn_2(oHB)_3Py_3$, based on Zinc)

Analysis Found: C,48.0; H,3.1; Cu,13.7; N,4.4; Zn,14.5 %

$C_{36}H_{27}Cu_2N_3O_9Zn_2$ Req: C,47.9; H,3.0; Cu,14.1; N,4.7; Zn,14.5 %

Infra Red (Nujol, cm^{-1}): 3000-2800(nujol); 1600; 1570; 1520;

1460 (nujol); 1400; 1380 (nujol); 1325; 1270; 1220; 1140; 1070; 1035; 880; 860; 840; 810; 760; 710 (sh); 700; 665; 580.

Solid 3: Yield 0.90g (22% if $Cu_3Zn_2(oHB)_4Py_3$, based on Zinc)

Analysis Found: C,47.5; H,3.2; Cu,17.2; N,4.1; Zn,11.7 %

$C_{43}H_{31}Cu_3N_3O_{12}Zn_2$ Req C,46.9; H,2.8; Cu,17.3; N,3.8; Zn,11.9 %

$C_{44}H_{32}Cu_3N_{3.2}O_{12}Zn_2$ Req C,47.2; H,2.9; Cu,17.0; N,4.0; Zn,11.7 %

Infra Red (Nujol, cm^{-1}): 3050 (w,sh); 3000-2800 (nujol); 1600 (s); 1565 (s); 1510; 1460 (nujol); 1445 (sh,s); 1400 (s); 1380 (nujol); 1330; 1265 (s); 1220 (w,sh); 1155 (sh); 1140; 1070; 1035; 880; 855; 840; 810 (w); 755 (s); 695 (s); 665; 580; 540 (w).

(b) To a solution of zinc 2-hydroxybenzoate (0.910g, 2.68mmol) in THF (15ml) and pyridine (0.22ml, 2.72mmol) was added a solution of copper(I) tert-butoxide (0.363g, 2.66mmol) in THF (20ml) producing a green solution. A pale green solid was formed on cooling this solution to -20°C which was separated by filtration (No 3 stick) and dried in vacuo. Concentration of the resulting clear green solution under reduced pressure (50% of solvent removed) and cooling to -20°C led to the formation of a lemon yellow solid which was collected as above. The solids were characterised as follows:

Solid 1: Yield 0.067g (11% if $Zn(oHB)Py_{0.4}$, based on Zinc)

Analysis Found: C,46.4; H,3.3; Cu,2.9; N,2.0; Zn,24.8 %

$C_9H_6N_{0.4}O_3Zn$ Req: C,46.4; H,2.6; Cu,0.0; N,2.4; Zn,28.0 %

Infra Red (Nujol, cm^{-1}): 3000-2800 (nujol); 1600 (s); 1565 (s); 1535; 1460 (sh, nujol); 1450 (s); 1400 (s); 1380 (sh, nujol); 1320;

1250(sh); 1240; 1160(sh); 1140; 1090(w); 1070(w); 1035; 880; 820; 810(sh); 765; 755(sh); 710; 700; 665; 585.

Solid 2: Yield 0.120g (12% if $Cu_2Zn_3(oHB)_4Py_3$, based on Zinc)

Analysis Found: C,46.5; H,2.9; Cu,10.8; N,3.6; Zn,15.7 %

$C_{43}H_{31}Cu_2N_3O_{12}Zn_3$ Req: C,46.7; H,2.8; Cu,11.5; N,3.8; Zn,17.8 %

Infra Red (Nujol, cm^{-1}): 3000-2800(nujol); 1600(s); 1575(s); 1520; 1460(sh, nujol); 1450; 1400(s); 1380(nujol); 1320; 1270; 1220; 1160(sh); 1140; 1070(w); 1035(w); 885; 840(w); 840; 810(w); 760; 715(w, sh); 700; 670; 585; 535(w, br).

(c) To a solution of zinc 2-hydroxybenzoate (1.007g, 2.96mmol) in THF (20ml) and pyridine (0.25ml, 3.09mmol) was added a solution of copper(I) tert-butoxide (0.810g, 5.92mmol) in THF (60ml) forming a yellow solution with precipitation occurring after 45ml of the copper solution had been added. The yellow solid so formed was separated by filtration (No 3 stick) and dried in vacuo. Concentration of the resulting clear yellow/green solution under reduced pressure (30% of solvent removed) and cooling to -20°C led to the formation of a yellow/green solid which was collected as above. The solids were characterised as follows:

Solid 1: Yield 0.538g (51% if $Cu_4Zn(oHB)_2OPy_{1.4}$ based on Copper)

Analysis Found: C,35.1; H,2.2; Cu,35.3; N,2.5; Zn,8.5 %

$C_{21}H_{15}Cu_4N_{1.4}O_7Zn$ Req: C,35.1; H,2.1; Cu,35.4; N,2.7; Zn,9.1 %

Infra Red (Nujol, cm^{-1}): 3050(w, sh); 3000-2800(nujol); 1600(s); 1575(s); 1515; 1485(w); 1460(sh, nujol); 1450(s); 1405(s); 1380(sh, nujol); 1325; 1265(s); 1220(w, sh); 1145; 1100(w);

1070; 1040; 885; 865; 840; 810; 760; 695; 670; 630; 590; 540(w); 460(w).

Solid 2: Yield 0.196g (8% if $Cu_2Zn_2(oHB)_3Py_2$, based on Copper)

Analysis Found: C,45.8; H,2.9; Cu,13.4; N,3.3; Zn,15.1 %

$C_{31}H_{22}Cu_2N_2O_9Zn_2$ Req: C,45.2; H,2.7; Cu,15.4; N,3.4; Zn,15.9 %

Infra Red (Nujol, cm^{-1}): 3050(w, sh); 3000-2800(nujol); 1600(s); 1575(s); 1520(s, m); 1460(sh, nujol); 1450(s); 1405(s); 1380(sh, nujol); 1320; 1270(s); 1220; 1160(sh); 1145(s); 1070; 1040; 890(s); 860(w); 840; 810(w); 760(s); 715(sh); 700(s); 670; 635(w); 590; 540(w); 455(w).

A second reaction was carried out with the same stoichiometry as above:

To a solution of zinc 2-hydroxybenzoate (1.331g, 3.92mmol) in THF (20ml) and pyridine (0.35ml, 4.32mmol) was added a solution of copper(I) tert-butoxide (1.071g, 7.837mmol) in THF (70ml) forming a yellow solution with precipitation occurring after 45ml of the copper solution had been added. About 2 minutes after the addition had been completed the mixture suddenly changed colour from yellow to dark green. The mixture was filtered (no 3 stick) giving a clear, pale green solution and a dark green solid which was dried in vacuo. Yield 1.736g (87% if $Cu_3Zn_2(oHB)_4Py_2$ based on Zinc). The solid was characterised as follows:

Analysis Found: C,44.2; H,2.8; Cu,19.0; N,2.8; Zn,13.2 %

$C_{38}H_{26}Cu_3N_2O_{12}Zn_2$ Req: C,44.6; H,2.6; Cu,18.7; N,2.7; Zn,12.8 %

Infra Red (Nujol, cm^{-1}): 3000-2800(nujol); 1600(s); 1570(s); 1560(sh);

1520(s); 1460(nujol); 1450(sh); 1400(sh); 1380(nujol); 1370(sh); 1325(w); 1265(s); 1250(sh); 1220(sh); 1140; 1070; 1040; 880; 860(w); 840; 810(w); 755(s); 710(sh); 700; 670; 630(w); 585; 535(w); 460(w).

Magnetic Moment μ_{eff} = 1.18BM.

(d) To a solution of zinc 2-hydroxybenzoate (0.502g, 1.48mmol) in THF (20ml) and pyridine (0.13ml, 1.61mmol) was added a solution of copper(I) tert-butoxide (0.808g, 5.91mmol) in THF (60ml) forming a yellow solution with precipitation occurring after 30ml of the copper solution had been added. The yellow solid so formed was separated by filtration (No 3 stick) and dried in vacuo causing it to darken in colour to green/yellow. Yield 0.824g (79% if $Cu_4Zn(oHB)_2OPy_{1.2}$ based on Copper). The solid was characterised as follows:

Analysis Found: C,33.7; H,2.4; Cu,34.7; N,2.3; Zn,9.3 %

$C_{20}H_{14}Cu_4N_{1.2}O_7Zn$ Req: C,34.2; H,2.0; Cu,36.2; N,2.4; Zn,9.3 %

Infra Red (Nujol, cm^{-1}): 3050(w, sh); 3000-2800(nujol); 1600(s); 1570(s); 1560(sh); 1515(s); 1460(sh, nujol); 1450(s); 1400(s); 1380(sh, nujol); 1320; 1265(s); 1220(w, sh); 1140; 1100(w); 1070(w); 1040; 1020(w); 885; 860(w); 835; 805(w); 755(s); 700(s); 670; 590; 540(w); 455(w).

7.3.4 Impregnation on to Alumina and Decomposition of Mixed Copper-Zinc Species

In exploratory studies, two of the materials prepared above were impregnated on to an alumina extrudate (supplied by ICI

Billingham) using their pyridine solutions. Interestingly, these solutions crystallised producing different compounds:

(a) Pyridine (5ml) was added to a sample of $Cu_4Zn(oHB)_2OPy_{1.2}$ (0.223g, from 7.3.3d) producing a dark green solution with some undissolved material. The solution was filtered (No 3 stick) to give a clear dark green solution and a small quantity of a pale brown solid. Before the green solution could be added to the alumina, needle crystals were formed. Thus, approximately half the solution was decanted off and added to dried alumina (1.10g) and the solvent gradually removed under reduced pressure. The resulting material was thermally decomposed by heating to 250°C in a nitrogen stream for 3 hours, followed by reduction in a N_2/H_2 (75:25) stream at 230°C for 2 hours. Small quantities of pyridine and carbon dioxide were evolved during the decomposition. The residue which contained only 2% copper and 1.2% zinc was tested, at ICI Billingham, and was shown to have an immeasurably small copper surface area by nitrous oxide titration.

The remaining solution was filtered and the small green, needle crystals were dried in vacuo. The apparently air stable product, $Cu(oHB)Py_2$, was characterised as follows:

<u>Analysis</u>	Found:	C,57.2; H,3.9; Cu,17.5; N,8.0 %
	$C_{17}H_{14}CuN_2O_3$ Req:	C,56.7; H,3.9; Cu,17.8; N,7.8 %

<u>Infra Red</u> (Nujol, cm^{-1}): 3000-2800(nujol); 1600(s); 1550(s); 1510(s); 1460(nujol); 1400(sh); 1380(nujol); 1340; 1255(s); 1220; 1140; 1070; 1040(w, sh); 1030; 1015(w); 890; 855; 835; 805; 760(s); 750(s); 700(s, sh); 695(s); 660; 630(w); 585.

(b) Pyridine (10ml) was added to a sample of $Cu_3Zn_2(oHB)_4Py_2$ (1.01g, from 7.3.3c) producing a dark green solution with some undissolved material. The solution was filtered (No 3 stick) to give a clear dark green solution and a material which looked like metallic zinc to the naked eye but under a microscope (x60) appeared to consist of small crystals. This material analysed as $Cu_4Zn_5(oHB)_5O_2Py_{10}$ and was characterised as follows:

Analysis Found: C,49.7; H,3.4; Cu,11.7; N,6.5; Zn,15.0 %

$C_{85}H_{70}Cu_4N_{10}O_{17}Zn_5$ Req: C,49.0; H,3.4; Cu,12.2; N,6.7; Zn,15.7 %

Infra Red (Nujol, cm^{-1}): 3050(w, sh); 3000-2800(nujol); 1600(s); 1555(s); 1515; 1460(sh, nujol); 1450(s); 1405(s); 1380(nujol); 1340(w); 1270(s); 1225; 1210(w, sh); 1155; 1145(sh); 1140(sh); 1070; 1045; 1030(sh); 1020; 1005(w, sh); 885; 860(w); 850; 830; 770;; 760(sh); 750(s); 710(sh); 700(s); 665; 640; 585; 540(w); 420(w).

Before the green solution could be added to the alumina needle crystals were formed. Thus, approximately half the solution was decanted off and added to dried alumina (2.33g) and the solvent gradually removed under reduced pressure. The resulting material was thermally decomposed by heating to 300°C in a nitrogen stream for 3 hours, followed by reduction in a N_2/H_2 (75:25) stream at 230°C for 2 hours. Small quantities of pyridine and carbon dioxide were evolved during the decomposition. The residue which contained only 2% copper and 1% zinc was tested, at ICI Billingham, on a microreactor and was shown to have almost no activity in methanol synthesis.

The remaining solution was filtered and the small green, needle crystals were dried in vacuo. The product analysed best for $Cu_3Zn(oHB)_3Py_6$, but there was evidence of inhomogeneity (microscopy x60) and the product was thought to consist of a mixture of $Cu(oHB)Py_2$ and ZnO (ir) and was characterised as follows:

Analysis Found: C,54.3; H,3.8; Cu,16.9; N,7.1; Zn,5.3 %
$C_{51}H_{42}Cu_3N_6O_9Zn$ Req: C,53.8; H,3.7; Cu,16.7; N,7.4; Zn,5.7 %
$C_{51}H_{42}Cu_3N_6O_{10}Zn$ Req: C,53.0; H,3.7; Cu,16.5; N,7.3; Zn,5.7 %

Infra Red (Nujol, cm^{-1}): 3000-2800(nujol); 1605(s); 1560(s); 1520; 1460(nujol); 1400(sh); 1380(nujol); 1340; 1260(s); 1220; 1155(w, sh); 1140(s); 1070; 1040(w, sh); 1035; 890; 860; 840; 810(w); 765; 750(s); 700(s); 670(w); 580(w).

7.3.5 Reactions of Copper(II) 2-(2-Methoxyethoxy)ethoxide and Zinc Hydroxycarboxylates

(a) To a solution of copper(II) 2-(2-methoxyethoxy)ethoxide (0.389g, 1.29mmol) in THF (60ml), was added a solution of zinc 2-hydroxybenzoate (0.435g, 1.28mmol) in THF (30ml) and pyridine (0.1ml, 1.24mmol). This caused the blue copper solution to turn green with a precipitate forming after about 20ml of the zinc solution had been added. The mixture was filtered (No 3 stick) and the pale green solid dried in vacuo. No further solid separated from the green solution despite concentration under reduced pressure (75% of solvent removed) and cooling to -20°C for several days. Yield 0.314g (51%, if $CuZn(oHB)_2Py$). The product which consisted of $CuZn(oHB)_2Py$ contaminated with Zn(oHB) was characterised as follows:

Analysis Found: C,45.7; H,3.0; Cu,11.3; N,2.1; Zn,14.6 %

$C_{19}H_{13}CuNO_6Zn$ Req: C,47.5; H,2.7; Cu,13.2; N,2.9; Zn,13.6 %

$C_7H_4O_3Zn$ Req: C,41.7; H,2.0; Cu, 0.0; N,0.0; Zn,32.4

Infra Red (Nujol,cm^{-1}): 3050(w,sh); 3000-2800(nujol; 1600(s); 1570(s); 1520(s); 1460(nujol); 1400(sh); 1380(nujol); 1320(sh); 1250(s); 1150; 1100(w); 1070; 1040; 890; 835; 805(w); 755(s); 700; 670; 640(w); 590; 530(w).

(b) To a slurry of anhydrous zinc tartrate (0.1959g, 0.918mmol) in THF (30ml) and pyridine (10ml) was added a solution of copper(II) 2-(2-methoxyethoxy)ethoxide (0.2775g, 0.919mmol) in THF and pyridine (1ml) and the resulting mixture stirred for 3 hours. The mixture was filtered (No 3 stick) yielding a clear green solution and a pale green solid (0.0859g) which contained zinc and copper in the ratio 38:1, and whose ir was identical to one of anhydrous zinc tartrate. The solution was concentrated (75% solvent removed) and cooled to -20°C for several days but no further solid separated.

CHAPTER 8

Summary Discussion and Suggestions for Future Work

This thesis has described work that was carried out to investigate the feasibility of using mixed metal alkoxides, carboxylates and hydroxycarboxylates as precursors to heterogeneous catalysts. The work was carried out as there is, at least for the methanol synthesis catalyst, a clear relationship between the structure of the precursor and the activity of the catalyst produced on calcination and the proposed precursors are likely to be more structurally ordered than the traditional basic carbonate precursors.

The importance and great complexity of industrial catalysts is evident from the literature review contained in chapter 2. The varied chemistry of alkoxides, carboxylates and hydroxycarboxylates is discussed in chapter 3 including the different forms of bridging observed in alkoxides (M-O-M) and carboxylates (M-O-C-O-M).

The use of co-precipitation and co-crystallisation reactions to prepare mixed metal salts was investigated. Some crystals of copper-zinc double salts resulted, for example $CuZn(O_2CH)_4$, but these were difficult to separate from crystals of the individual salts which formed simultaneously. However further study in this area is worthwhile, for example the use of pH control may lead to better results.

The thermal decomposition of mixtures of metal alkoxides with carboxylates of another metal were different to the decompositions of the individual compounds. This was particularly evident in the decomposition of copper(II) formate with zinc methoxide as a substantial quantity of methyl formate was evolved (approximately 25% yield) and no copper mirror was formed. The main problem encountered was one of the copper sintering which was exemplified by the XPS and copper surface area measurements. The use of an oxidising atmosphere and a lower temperature in the decomposition so as to produce copper oxides which could then be carefully reduced may help to prevent this sintering and thus increase the catalytic activity. A second way to reduce the sintering would be to impregnate the alkoxide and carboxylate on to a support, such as alumina, prior to decomposition but the low solubilities of the simple alkoxides of copper and zinc precludes this.

The reaction of soluble copper alkoxides (e.g. copper(I) tert-butoxide) with soluble zinc hydroxycarboxylates (e.g. zinc 2-hydroxybenzoate) produced, apparently mixed metal compounds (e.g. $CuZn(O_2CC_6H_4O)_2.Py$). However the chemistry here was very complex and further study is necessary to clarify the observations of chapter 7. Nonetheless this method offers great potential for preparing mixed metal compounds of varying metal stoichiometry and spacing. As stated in chapter 7 the use of zinc alkoxides and copper hydroxycarboxylates may lead to further progress in this area.

The work described in this thesis, whilst not including the preparation of a new catalyst, provides much information for other workers wishing to investigate the principle of using mixed metal alkoxides, carboxylates and hydroxycarboxylates as catalyst precursors and as such I hope that it proves useful.

REFERENCES

1. Chinchen, G.C., Denny, P.J., Parker, D.G., Short, G.D., Spencer, M.S., Waugh, K.C., Whan, D.A., Prepr. Amer. Chem. Soc. Div. Fuel Chem., 1984, 29, 178.
2. Bridger, G.W., Spencer, M.S., in The Catalyst Handbook, 2nd Edition, Ed. Twigg, M.V., Wolfe, 1989, Chapters 1 and 9.
3. Waller, D., Stirling, D., Stone, F.S., Spencer, M.S., RSC Faraday Discussion No. 87, Liverpool, 1989, 107.
4. Young, K., PhD. Thesis, University of Durham, 1989.
5. Hauptman, Z.V., MacBride, J.A.H., Wade, K., Unpublished studies in this Laboratory.
6. Bond, G.C., Principles of Catalysis, The Chemical Society, 1972.
7. Bond, G.C., Catalysis by Metals, Academic Press, 1962.
8. Robertson, A.J.B., Catalysis of Gas Reactions by Metals, Logus Press Ltd., 1970.
9. Characterisation of Catalysts, Ed. Thomas, J.M., Lambert, R.M., Wiley, 1980.
10. Thomas, J.M., Angew. Chem. Int. Ed. Engl. Adv. Mater. 1989, 28(8,9), 1079.
11. Berzelius, J.J., Annls. Chim. Phys., 1836, 61, 146; Rideal, E.K., Taylor, H.S., Catalysis in Theory and Practice, Macmillan, 1919.
12. Bart, J.C.J., Sneeden, R.P.A., Catal. Today., 1987, 2(1), 1.
13. ICI Ltd. Fr. Pat., 1 489 682, 1968; Chem. Abstr., 1968, 69, 35412.
14. Cornthwaite, D., (To ICI Ltd.), Brit. Pat. 1 296 212, 1972; Chem. Abstr. 1973, 78, 71404.
15. Cornthwaite, D., (To ICI Ltd.), U.S. Pat., 3 923 694, 1975; Chem.

Abstr., 1976, 84, 127 216.

16. Klier, K., Advances in Catalysis, 1982, 31, 243.

17. Porta, P., De Rossi, S., Ferraris, G., Lo Jacono, M., Minelli, G., Moretti, G., J. Catal., 1988, 109, 367.

18. Sengupta, G., Das, D.P., Ketchik, S.V., Kundu, M.L., Dutta, S., Roy, S.K., Sahay, R.N., Mishru, K.K., Appl. Catal., 1989, 55, 165.

19. Marsden, W.L., Wainwright, M.S., Friedrich, J.B., Ind. Eng. Chem., Prod. Res. Dev., 1980, 19, 551; Chem. Abstr., 1980, 93, 203 988.

20. Friedrich, J.B., Wainwright, M.S., Young, D.J., J. Catal., 1983, 80, 1.

21. Friedrich, J.B., Wainwright, M.S., Young, D.J., J. Catal., 1983, 80, 14.

22. Bridgewater, A.J., Wainwright, M.S., Young, D.J., Orchard, J.P., Appl. Catal., 1983, 7, 369.

23. Baglin, E.G., Atkinson, G.B., Nicks, L.J., Ind. Eng. Chem., Prod. Res. Dev., 1981, 20, 87; Chem. Abstr., 1981, 94, 139 134.

24. Daly, F.P., J. Catal., 1984, 89, 131.

25. Short, G.D., Jennings, J.R., Jap. Pat, 59/ 116 238, 1984; Chem. Abstr., 1984, 101, 194 140.

26. Nix, R.M., Judd, R.W., Lambert, R.M., Jennings, J.R., Oeen, G., J. Catal., 1989, 118, 175.

27. Herman, R.G., Klier, K., Simmons, G.W., Finn, B.P., Bulko, J.B., J. Catal, 1979, 56, 407.

28. Kau, L.S., Hodgson, K.O., Solomon, E.I., J. Am. Chem. Soc., 1989 111, 7103; Didziulis, S.V., Butcher, K.D., Cohen, S.L., Solomon, E.I., J. Am. Chem. Soc., 1989, 111, 7110.

29. Bowker, M., Hadden, R.A., Houghton, H., Hyland, J.N.K., Waugh, K.C.,

J. Catal., 1988, 109, 263.

30. Chinchen, G.C., Denny, P.J., Parker, D.G., Spencer, M.S., Appl. Catal., 1987, 30, 333.

31. Pan, W.X., Cao, R., Roberts, D.L., Griffin, G.L., J. Catal, 1988, 114, 440.

32. Chinchen, G.C., Waugh, K.C., Whan, D.A., Appl. Catal., 1986, 25, 101.

33. Parris, G.E., Klier, K., J. Catal., 1986, 97, 374.

34. Burch, R., Chappell, R.J., Golunski, S.E., Catal. Lett., 1988, 1, 439.

35. Duprex, D., Ferhat-Hamida, Z., Bettahar, M.M., J. Catal., 1990, 124, 1.

36. Frost, J.C., Nature, 1988, 334, 577.

37. Bradley, D.C., Mehrotra, R.C., Gaur, D.P., Metal Alkoxides, Academic Press, 1978.

38. Chisholm, M.H., Rothwell, I.P., in Comprehensive Coordination Chemistry, Ed. Wilkinson, G.W., Gillard, R.D., McCleverty, J.A., Pergamon Press, 1987, Volume 2, Chapter 15.3, p335.

39. Ethyl Corp., Br. Pat. 727 923, 1955; Chem. Abstr., 1956, 50, 5018

40. Lochmann, L. Lim, D., Coupek, J., Ger. Pat., 2 035 260, 1971; Chem. Abstr., 1971, 74, 87355.

41. Lukasik, J., Maij, S.L., Strauss, I., Piekos, R., Rocz. Chem., 1970, 44(9), 1675.

42. Cohen, C.A., U.S. Pat., 2 287 088, 1943; Chem. Abstr., 1943, 37, 141.

43. Banait, J.S., Pahil, P.K., Synth. React. Inorg. Met. -Org. Chem. 1986, 16(9), 1217.

44. Banait, J.S., Pahil, P.K., Polyhedron, 1986, 5(11), 1865.

45. Shreider, V.A., Turevskaya, E.P., Koslova, N.I., Tunova, N.A.,

Inorg. Chim. Acta., 1981, 53, L73.

46. Szilard, B., Z. Electrochem., 1906, 12, 393; J. Chem. Soc., Abstracts, 1906, 90(1), 621.

47. Jennings, J.S., Wardlaw, W., Way, W.J.R., J. Chem. Soc., 1936, 637.

48. Varma, I.D., Mehrotra, R.C., J. Indian Chem. Soc., 1961, 38, 147.

49. Nelles, J., U.S. Pat. 2 187 821, 1939; Chem. Abstr., 1940, 34, 3764.

50. Cullinane, N.M., Chard, S.J., Nature, 1949, 164, 710.

51. Cullinane, N.M., Chard, S.J., Price, G.F., Millward, B.B., J. Soc. Chem. Ind., London, 1950, 69, 538; Chem. Abstr., 1951, 45, 7950.

52. Reagan, W.J., Brubaker, C.H., Inorg. Chem. 1970, 9, 827.

53. Bradley, D.C., Caldwell, E.V., Wardlaw, W., J. Chem. Soc., 1957, 4775.

54. Mehrotra, R.C., Arora, M., Z. Anorg. Allg. Chem., 1969, 370, 300.

55. Bradley, D.C., Chakravarti, B.N., Chatterjee, A.K., Wardlaw, W., Whitey, A., J. Chem. Soc., 1958, 99.

56. Kapoor, R.N., Mehrotra, R.C., J. Am. Chem. Soc., 1960, 82, 3495.

57. Backer, R.H., J. Am. Chem. Soc., 1938, 60, 2673.

58 Mehrotra, R.C., J. Am. Chem. Soc., 1954, 76, 2266.

59. Coates, G.C., Ridley, D., J. Chem. Soc., 1965, 1870.

60. Coates, G.C., Roberts, P.D., J. Chem. Soc.(A), 1967, 1233.

61. Caldin, E.F., Long, G., J. Chem. Soc., 1954, 3737.

62. Thomas, I.M., Can. J. Chem., 1961, 39, 1386.

63. Turova, N. Ya., Kozunov, V.A., Yanovskii, A.I., Bokii, N.G., Struchkov, Yu.T., Tarnopolskii, B.L., J. Inorg. Nucl. Chem., 1979, 41, 5.

64. Bradley, D.C., Mehrotra, R.C., Swanwick, J.D., Wardlaw, W.,

J. Chem. Soc., 1953, 2025

65. Martin, R.L., Winter, G., J. Chem. Soc., 1961, 2947.

66. Brubaker, C.H., Wicholas, M., J. Inorg. Nucl. Chem., 1965, 27, 59.

67. Singh, J.V., Baranwal, B.P., Mehrotra, R.C., Z. Anorg. Allg. Chem., 1981, 477, 235.

68. Adams, R.W., Barraclough, C.G., Martin, R.L., Winter, G., Aust. J. Chem., 1967, 20, 2351.

69. Wells, A.F., J. Chem. Soc., 1947, 1670.

70. Tsuda, T., Hashimoto, T., Saegusa, T., J. Am. Chem. Soc., 1972, 94(2), 658.

71. Greiser, T., Weiss, E., Chem. Ber., 1976, 109, 3142.

72. Dahl, L.F., Davies, G.L., Wampler, D.L., West, K., J. Inorg. Nucl. Chem., 1962, 24, 357.

73. Weiss, E., Alsdorf, H., Kuhr, H., Angew. Chem., Int. Ed. Engl., 1967, 6, 801.

74. Shearer, H.M.M., Spencer, C.B., Chem. Comm., 1966, 194.

75. Bradley, D.C., Adv. Inorg. Chem. Radiochem. 1972, 15, 267.

76. Bradley D.C. in Inorganic Polymers, Ed. Stone, F.G.A., Graham, W.A.G., Academic Press, 1962, Chapter 7, p411.

77. Ouhadi, T., Hamitou, A., Jerome, R., Teyssie, Ph., Macromol., 1976, 9(6), 927.

78. Ouhadi, T., Bioul, J.P., Stevens, C., Warin, R., Hocks, L., Teyssie, Ph., Inorg. Chim. Acta, 1976, 19, 203.

79. Teyssie, Ph., Bioul, J.P., Hocks, L., Ouhadi, T., Chemtech, 1977, 7, 192.

80. Panday, K.C., Mehrotra, R.C., Z. Anorg. Allg. Chem., 1956, 286, 291.

81. Young, D.W., Kellog, H.B., U.S. Pat., 2 440 498, 1948; Chem. Abstr.,

1948, 42, 5268.

82. Rehberg, C.E., Org. Synth., 1946, 26, 18.

83. Rehberg, C.E., Fisher, C.H., J. Org. Chem., 1947, 12, 226.

84. Caldwell, J.R., U.S. Pat., 2 720 502, 1955; Chem. Abstr., 1956, 50, 2204.

85. Caldwell, J.R., Wellman, J.W., U.S. Pat., 2 720 504, 1955; Chem. Abstr., 1956, 50, 2205.

86. Caldwell, J.R., Reynolds, D.D., U.S. Pat.,2 720 506, 1955; Chem. Abstr., 1956, 50, 2205.

87. Farbenfabriken Bayer A.G., Br. Pat., 734 114, 1955; Chem. Abstr., 1956, 50, 7123.

88. Boyd, T., (To Monsanto Chemical Co.), U.S. Pat., 2 716 656, 1955; Chem. Abstr. 1956, 50, 1372

89. Flaschen, S.S., J. Am. Chem. Soc., 1955, 77, 6194.

90. Levene, L., Thomas, I.M., U.S. Pat., 3 640 093, 1972; Chem. Abstr., 1972, 77, 167 990.

91. Thomas, I.M., U.S.Pat., 3 799 754, 1974; Chem. Abstr., 1974, 81, 110 443.

92. Goel, S.C., Kramer, K.S., Gibbons, P.C., Buhro, W.E., Inorg. Chem., 1989, 19, 1.

93. Horowitz, H.S., McLain, S.J., Sleight, A.W., Druliner, J.D., Gai, P.L., VanKavelaar, M.J., Wagner, J.L., Biggs, B.D., Poon, S.J., Science, 1989, 243, 66.

94. Mehrotra, R.C., Bohra, R. Metal Carboxylates, Academic Press, 1983.

95. Oldham, C., in Comprehensive Coordination Chemistry, Ed. Wilkinson, G.W., Gillard, R.D., McCleverty, J.A., Pergamon Press, 1987, Volume 2, Chapter 15.6, p435.

96. Martin, R.L., Waterman, H., J. Chem. Soc., 1957, 2545.

97. Figgis, B.N., Martin, R.L., J. Chem. Soc., 1956, 3837.

98. Baillie, M.J., Brown, D.H., Moss, K.C., Sharp, D.W.A., J. Chem. Soc., A, 1968, 3110.

99. Smith, G.H., Pomeroy, H.H., McGee, C.G., Mysels, K.J., J. Am. Chem. Soc., 1948, 70, 1053.

100. McBain, J.W., McClatchie, W.L., J. Am. Chem. Soc., 1932, 54, 3266.

101. Hood, G.C., Ihde, A.J., J. Am. Chem. Soc., 1950, 72, 2094.

102. Zenina, G.V., Sheverdina, N.I., Kocheshkov, K.A., Dokl. Akad. Nauk. SSSR, 1970, 195(1), 96; Chem. Abstr., 1971, 74, 100 147.

103. Vasenta, E.N., Srivastava, G., Mehrotra, R.C., Inorg. Chim. Acta., 1978, 26, 47.

104. Banait, J.S., Pahil, P.K., Polyhedron, 1985, 4(6), 1031.

105. Prout, C.K., Armstrong, R.A., Carruthers, J.R., Forrest, J.G., Murray-Rust, P. Rossotti, F.J.C., J. CHem. Soc. A, 1968, 2791.

106. Catterick, J., Thornton, P., Adv. Inorg. Chem. Radiochem., 1977, 20, 291.

107. Oldham, C., Prog. Inorg. Chem., 1968, 10, 223.

108. Zachariasen, W.H., J. Am. Chem. Soc., 1940, 62, 1011.

109. Padmanabhan, V.M., Acta. Cryst., 1958, 11, 896.

110. Van Niekerk, J.N., Schoening, F.R.L., Talbot, J.H., Acta. Cryst., 1953, 6, 720.

111. De Meester, P., Fletcher, S.R., Skapski, A.C., J. Chem. Soc. Dalton, 1973, 2575.

112. Kiriyama, R., Ibamato, H., Matsuo, K., Acta. Cryst., 1954, 7, 482.

113. Barclay, G.A., Kennard, C.H.L., J. Chem. Soc., 1961, 3289; Burger, N., Fuess, H., Solid State Comm., 1980, 34, 699.

114. Garaj, J., Langfelderova, H., Lundgren, G., Gazo, J., Collect. Czech. Chem. Commun. 1972, 37(10), 3181.

115. Pedrosa de Jesus, J.D., in Comprehensive Coordination Chemistry, Ed. Wilkinson, G.W., Gillard, R.D., McCleverty, J.A., Pergamon Press, 1987, Volume 2, Chapter 15.7, p461.

116. Singh, K.D., Jain, S.C., Sakore, T.D., Biswas, A.B., Acta. Cryst., Sect. B, 1975, 31, 990.

117. Hanic, V.F., Michalov, J., Acta. Cryst., 1960, 13, 299.

118. Klug, H.P., Alexander, L.E., Sumner, G.G., Acta. Cryst., 1958, 11, 41.

119. Deacon, G.B., Organometallic Chem. Rev. A, 1970, 5, 355.

120. Finar, I.L., Organic Chemistry, 2nd Ed., Longmans Green & Co., 1956, Volume 1, p120.

121. Mu, J., Perlmutter, D.D., Thermochimica Acta, 1981, 49, 207.

122. Maiti, G.C., Kundu, M.L., Ghosh, S.K., Banerjee, B.K., Therm. Anal. Proc. Int. Conf. 1974, Publ 1975, 2, 395.

123. Baraldi, P., Spectrochim. Acta., 1979, 35A, 1003.

124. Khokhlacheva, N.M., Tolstay, M.A., Poluden, R.I., Moldovanov, Y.I., Zharinov, A.V., Deposited Doc., 1980, VINITI, 4006-80 (see Chem. Abstr., 1982, 96: 147 460)

125. Khimchenko, Y.I., Vasilenko, V.P., Radkevich, L.S., Myalkovskii, V.V., Chubar, T.V., Cheyoryan, V.M., Poroshkovaya Metal., 1977, 5, 7.

126. Vecher, A.A., Dalidovisch, S.V., Gusev, E.A., Thermochim. Acta., 1985, 89, 383

127. Lazerko, G.A., Torkailo, E.M., Zaretskii, M.V., Russ. J. Inorg. Chem., 1984, 29(5), 694; Trans. from Zh. Neorg. Khim., 1984, 29, 1214.

128. Khimchenko, Y.I., Khvorav, M.M., Chirkov, A.S., Kosorukov, A.A., Poroshkovaya Metal., 1983, 5, 14.

129. Sharov, V.A., Nikonenko, E.A., Koord. Khim., 1980, 6(10), 748.

130. Buono, F.J., Feldman, M.L., Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., 1979, Volume 8, p34.

131. Rissanen, K., Valkonen, J., Kokkonen, P., Leskelä, M., Acta. Chem. Scand., 1987, A41, 299.

132. Calvin, M., J. Am. Chem. Soc., 1939, 61, 2230.

133. Bogdanova, E.N., Neftepereab Nefleklum, 1973, 59; Chem. Abstr., 1974, 80, 135 209

134. Lehmann, H., Riethmayer, S., (To Industrie Automaton G.m.b.H. & Co.), Ger. Offen, 2 503 871, 1976; Chem. Abstr., 1976, 85, 162122.

135. Ogawa, H., Jap Pat. 71 22740, 1971; Chem. Abstr., 1972, 77, 91071.

136. Trotz, S.I., Pitts, J.J., Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., 1981, Volume 13, p223

137. Davis, G.M., U.S. Pat., 2 945 051, 1960; Chem. Abstr., 1960, 54, 20 253

138. Isacoff, H., Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., 1979, Volume 7, p143

139. Tawada, A., Jpn. Kokai, 93132, 1978; Chem. Abstr., 1978, 89, 223 201.

140. Dalvi, B.D., Chavan, A.M., J. Therm. Anal. 1978, 14, 331.

141. Ogata, T., Osaki, K. Taga, T., Bull. Chem. Soc. Jpn., 1977, 50, 1674.

142. Greenwood, N.N., Ionic Crystals: Lattice Defects and Non-Stoichiometry, Butterworths, 1968.

143. Hoskins, B.F., Robson, R., J. Am. Chem. Soc., 1990, 112, 1546.

144. Handbook of Chemistry and Physics, 63rd Edition, Ed. Weast, R.C., CRC Press, Florida.

145. Palmer, W.G., Experimental Inorganic Chemistry, Cambridge University Press, 1970, p213.

146. Viswamitra, M.A., J. Chem. Phys., 1962, 37, 1408

147. Cox, R.J., Wade, K., Unpublished Studies in this Laboratory.

148. Brzyska, W., Bubela, G., Biul. Lubel. Tow. Nauk., Mat-Fiz. Chem. 1982, 24(1), 15. Chem. Abs., 1984, 102, 104 976.

149. Brzyska, W., Falisz, W., Biul. Lubel. Tow. Nauk., Mat-Fiz. Chem. 1984, 24(2), 165. Chem. Abs., 1984, 102, 214 061.

150. Pajunen, A., Nasakkala, E., Finn. Chem. Lett., 1977, 4-5, 104.

151. Sigma-Aldrich Library of Chemical Safety Data, 2nd Edition, Ed. Lenga, R.E., 1988.

152. Edwards, D.A., Richards, R., JCS Dalton, 1973, 2463.

153. Sidgwick, N.V., Chemical Elements and Their Compounds, Vol 1, Oxford, 1951, p126.

154. Addison, C.C., Hathaway, B.J., J.Chem. Soc., 1958, 3099.

155. Cotton,F.A., Wilkinson,G., Advanced Inorganic Chemistry, Fifth Edition Wiley, 1980, p600.

156. Practical Surface analysis by Auger and X-ray Photoelectron Spectroscopy. Ed. Briggs,D.,Seah,M.P., 1983, Wiley, p477.

157 Chinchen, G.C., Hay, C.M., Vandervell, H.D., Waugh, K.C., J. Catal., 1987, 103, 79.

158. Goel, S.C., Kramer, K.S., Gibbons, P.C., Buhro, W.E., Inorg. Chem., 1989, 19, 1.

159. Hathaway, B.J., in Comprehensive Coordination Chemistry, Ed. Wilkinson, G.W., Gillard, R.D., McCleverty, J.A., Pergamon Press, 1987, Volume 5, Chapter 53, p553.

160. Marr, G., Rockett, B.W., Practical Inorganic Chemistry, Van

Nostrand Reinhold Co., London, 1972, p372.

161. Keller, R.N., Wycoff, H.D., Inorg. Synth., 1946, 2, 1.

Appendix 1: Experimental Techniques

1. General

The majority of compounds synthesised during the course of this study and many of the starting materials are sensitive to atmospheric exposure, through hydrolysis, or oxidation, or both. All operations on such compounds were therefore performed under an atmosphere of dry nitrogen: glassware was either oven- or flame-dried before purging with dry nitrogen; solvents and solutions of reagents were transferred by syringe against a counter-flow of dry nitrogen; filtrations made use of standard filter stick techniques; apparatus manipulations were minimised, and when necessary were made against a counter-flow of dry nitrogen; air sensitive solids were handled in a glove box.

2. Gases

Two sources of nitrogen gas were used: the boil-off from a tank of liquid nitrogen - the gas was piped to the laboratory after it had been passed through a deoxygenation plant, and cylinders of BOC "white spot" nitrogen. BOC reforming gas (N_2/H_2 75:25) was piped to the laboratory from an outside cylinder store. The gases were dried at the bench by passage through columns packed with A4 molecular sieve and phosphorus pentoxide.

3. Glove Boxes

Compounds of limited air sensitivity were handled in a glove box of simple design, the dry nitrogen atmosphere of which was maintained by continuous recycling through columns packed with A4 molecular sieve and phosphorus pentoxide. Compounds of more extreme air sensitivity were handled in a Faircrest glove box purged with BOC "white spot" nitrogen, the atmosphere of which was continually passed through columns of: A4 molecular sieve to remove water (regenerated periodically by heating under vacuum); copper catalyst (a copper on zeolite catalyst is used although its action is stoichiometric rather than catalytic) to remove oxygen (regenerated periodically by heating in a stream of reforming gas: N_2/H_2, 75/25) and activated charcoal to remove other impurities.

4. Solvents

Most solvents used were dried by standard methods before use: hydrocarbons over freshly extruded sodium wire; THF by refluxing with potassium, using benzophenone as indicator and distilling onto extruded sodium wire (stored under dry nitrogen); methanol by refluxing with magnesium turnings and iodine (stored under dry nitrogen). Pyridine was used as supplied in an Aldrich "sure-seal" bottle (water <0.005%).

5. pH Measurement

Measurement of pH was effected using a Jenway 3020 pH meter fitted with a Jenway PCP 505 combination electrode and an automatic temperature compensation probe.

6. Thermal Decompositions

Thermal decompositions were carried out in a furnace consisting of resistance wire wound on silica tubing (diameter 30mm, length 220mm) encased in a further piece of silica tubing (diameter 50mm, length 220mm). Power was supplied to the furnace via a Eurotherm 815P programmable temperature controller protected by an independent, adjustable, thermal cut out.

Two designs of pyrolysis tube were used: one for vacuum work (Fig A.1) the other (Fig A.2) enabling decompositions to be carried out under streams of various gases at varying pressures (all less than or equal to one atmosphere).

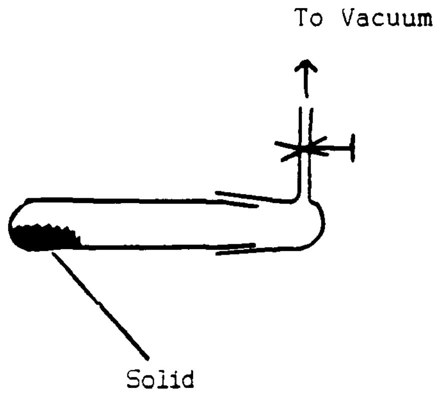


Fig A.1

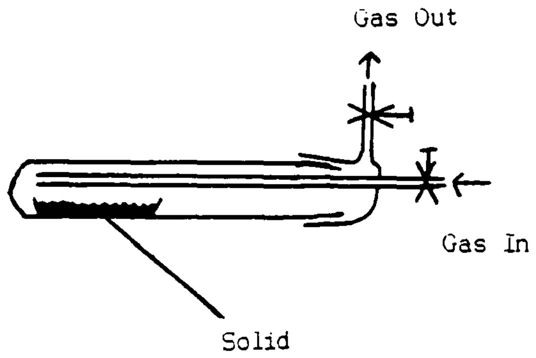


Fig A.2

Volatile products were collected in a liquid nitrogen trap (several, in series, in the case of gas stream decompositions). These were fractionated using a standard train with the traps being cooled by liquid nitrogen (-196°C) and either methanol/liquid nitrogen slush (-98°C) or acetone/dry ice slush (-78°C). The volatiles were identified by gas phase infra red spectroscopy (ir, in main text) and by gas chromatography mass spectroscopy (gcms, in the main text) and were quantified by volume/pressure measurements or by collection and weighing depending on their volatility. The residues were treated as being air sensitive.

7. Analysis

Carbon, hydrogen and nitrogen were determined on a Carlo Erba Strumentazione Elemental Analyser (Model 1106). Metals were determined on a Perkin Elmer 5000 Atomic Absorption Spectrophotometer. Halogens were determined by oxygen flask combustion or acid digestion followed by potentiometric titration. Air sensitive samples were sealed in pre weighed tin or gelatine capsules in a glove box.

8. Infra Red

Infra red spectra, in the range 4000-250 cm^{-1}, were recorded on Perkin Elmer 457 or 577 grating spectrometers. Samples were mounted as nujol mulls or contact films between KBr plates or as KBr discs. In the case of liquids suspected of containing water, KRS-5 plates were used. Gas phase spectra were recorded using a 10cm KBr gas cell.

9. Mass Spectroscopy

Mass spectra were recorded on a V.G. 7070E Analytical Organic Mass Spectrometer operating at 70eV. Chemical ionisation (CI) spectra were recorded using ammonia as reagent gas. Source temperatures of 150-250°C were used and samples were introduced by either direct insertion or via a glc fitted with a Hewlitt Packard Cross Linked Methyl Silicone Capillary Column (inside diameter, 0.2mm; length, 25m).

10. Nuclear Magnetic Resonance Spectroscopy

N.M.R. spectra were recorded on a Brüker AC250 Fourier Transform Spectrometer using TMS as internal reference for ^1H spectra and phenyllithium as an external reference for ^7Li spectra. Deuterated solvents were used as supplied and stored under dry nitrogen.

11. X-Ray Powder Diffraction

X-ray powder photographs were recorded using a Philips X-ray generator (PW1009/80) fitted with a CuK_α tube and two Debye-Scherrer powder cameras. The X-ray beams were controlled by a Hiltonbrooks DG2-2 window shutter controller. Samples were presented as fine powders loaded in 0.5mm Lindemann capillaries.

12. Transmission Electron Microscopy

TEM's were recorded on a Phillips EM400T instrument in which samples were bombarded with high energy electrons under an accelerating voltage of 100kV, the images being preserved on Kodak 83mm electron microscope film. Samples were prepared by placing one to two drops of an ethanol suspension of the material to be examined on Cu or Al grids (3mm) and allowing the ethanol to evaporate.

13. X-Ray Photoelectron Spectroscopy

XPS were recorded on a Kratos ES300 surface analysis instrument using MgK_α (1253.6eV) radiation. Spectra were aquired in the Fixed Analyser Transmission (FAT) mode. The take off angle between electron exit and the sample was kept constant at 60°.

Appendix 2: Research Colloquia, Seminars Lectures, Meetings and Conferences Between October 1987 and August 1990

(a) Colloquia, Seminars and Lectures Given by Invited Speakers

15.10.87* WINTER, Dr. M.J., University of Sheffield,
Pyrotechnics - A Demonstration Lecture.

22.10.87* GRAY, Prof. G.W., University of Hull,
Liquid Crystals and Their Applications.

29.10.87* VAN ROSE, Mrs S., Geological Museum,
Chemistry of Volcanoes.

4.11.87 MAPLETOFT, Mrs M., Durham Chemistry Teachers Centre,
Salters' Chemistry.

5.11.87* BUTLER, Dr. A.R., University of St. Andrews,
Chinese Alchemy.

12.11.87 SEEBACH, Prof. D., E.T.H. Zurich,
From Synthetic Methods to Mechanstic Insight.

26.11.87 WILLIAMS, Dr. D.H., University of Cambridge,
Molecular Recognition.

11.87 DAVIDSON, Dr. J., Herriot-Watt Universty,
Metal Promoted Oligomerisation of Alkynes.

3.12.87 HOWARD, Dr. J., ICI Wilton,
Chemistry of Non-Equilibrium Processes.

10.12.87* LUDMAN, Dr., C.J., University of Durham,
Explosives - A Demonstration Lecture.

16.12.87 SWART, Mr. R.M., ICI,
The Interaction of Chemicals With Lipid Bilayers.

19.12.87* SAMMES, Prof. P.G., Smith, Kline and French,
Chemical Aspects of Drug Development.

21. 1.88* PALMER, Dr. F., University of Nottingham,
Luminescence - A Demonstration Lecture.

28. 1.88* CAIRNS-SMITH, Dr. A., Glasgow University,
Clay Minerals and the Origin of Life.

9. 2.88 LACEY, Mr., Durham Chemistry Teachers' Centre
Double Award Science.

11. 2.88* TURNER, Prof. J.J., University of Nottingham,
Catching Organometallic Intermediates.

18. 2.88* BORER, Dr. K., University of Durham Ind. Research Labs,
The Brighton Bomb - A Forensic Science View.

25. 2.88* UNDERHILL, Prof. A., University of Bangor,
Molecular Electronics.

3. 3.88 GRAHAM, Prof. W.A.G., University of Alberta, Canada,
Rhodium and Iridium Complexes in the Activation of
Carbon - Hydrogen Bonds.

7. 3.88 KOCH, Prof. H.F., Ithaca College, U.S.A.,
Does the E2 Mechanism Occur in Solution?

16. 3.88 BOSSONS, L., Durham Chemistry Teachers' Centre,
GCSE Practical Assessment.

7. 4.88 HARTSHORN, Prof. M.P., University of Canterbury, N.Z.
Aspects of Ipso - Nitration.

13. 4.88 ROBERTS, Mrs. E., SATRO Officer for Sunderland,
Talk - Durham Chemistry Teachers' Centre - "Links
Between Industry and Schools."

18. 4.88 NIETO DE CASTRO, Prof. C.A., University of Lisbon and
Imperial College,
Transport Properties of Non - Polar Fluids.

25. 4.88* BIRCHALL, Prof. D., I.C.I. Advanced Materials,
Environmental Chemistry of Aluminium.

27. 4.88 RICHARDSON, Dr. R., University of Bristol,
X - Ray Diffraction from Spread Monolayers.

27. 4.88 ROBINSON, Dr. J.A., University of Southhampton,
Aspects of Antibiotic Biosynthesis.

28. 4.88 PINES, Prof. A., University of California, U.S.A.,
Some Magnetic Moments.

11. 5.88* McDONALD, Dr. W.A., I.C.I. Wilton,
Liquid Crystal Polymers.

11. 5.88 SODEAU, Dr. J., University of East Anglia,
Durham Chemistry Teachers' Centre Lecture -
"Spray Cans, Smog and Society."

8. 6.88 MAJORAL, Prof. J.P., Universite Paul Sabatier,
Stabilisation by Complexation of Short-Lived Phosphorus
Species.

29. 6.88 JONES, Dr. M.E., Durham Chemistry Teachers' Centre,
GCSE Chemistry Post-mortem.

29. 6.88 OLAH, Prof. G.A., University of Southern California,
New Aspects of Hydrocarbon Chemistry.

6. 7.88 JONES, Dr. M.E., Durham Chemistry Teachers' Centre,
GCE Chemistry A Level Post-mortem.

6.10.88 SCHMUTZLER, Prof. R., Techische Universitat Braunschweig,
Flourophosphines Revisited - New Contributions to an Old Theme.

18.10.88 BOLLEN, Mr. F., Durham Chemistry Teachers' Centre,
Lecture about the use of SATIS in the classroom.

18.10.88 DINGWALL, Dr. J., Ciba Geigy,
Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products.

18.10.88* LUDMAN, Dr. C.J., University of Durham,
The Energetics of Explosives.

21.10.88 VON RAGUE SCHLEYER, Prof. P., Universitat Erlangen Nurnberg,
The Fruitful Interplay Between Calculational and Experimental Chemistry.

27.10.88* REES, Prof. C.W., Imperial College London,
Some Very Hetreocyclic Compounds.

9.11.88 SINGH, Dr. G., Tesside Polytechnic,
Towards Third Generation Anti-Leukaemics.

10.11.88* CADOGAN, Prof. J.I.G., British Petroleum,
From Pure Science to Profit.

16.11.88 McLAUCHLAN, Dr. K.A., University of Oxford,
The Effect of Magnetic Fields on Chemical Reactions.

24.0.88 BALDWIN & WALKER, Drs. R.R. & R.W., Hull University,
Combustion: Some Burning Problems.

1.12.88* SNAITH, Dr. R., Cambridge University,
Egyptian Mummies: What, Where, Why and How?

9.12.88 JÄGER, Dr. C., Friedrich-Schiller University GDR,
NMR Investigations of Fast Ion Conductors of the Nasicon Type.

14.12.88 MORTIMER,Dr. C., Durham Chemistry Teachers Centre,
The Hindenberg Disaster - An Excuse for Some Experiments.

12.88 HARDGROVE, Dr. G., St. Olaf College, USA,
Polymers in the Physical Chemistry Laboratory.

25. 1.89 HARWOOD, Dr. L., Oxford University,
Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry Under Pressure

26. 1.89 JENNINGS, Prof. R.R., Warwick University,
Chemistry of the Masses.

1. 2 89 CRESSEY & WATERS, Messrs D & T, Durham Chemistry Teachers Centre
GCSE Chemistry 1988: "A Coroner's Report"

2. 2.89* HALL, Prof. L.D., Addenbrook's Hospital, Cambridge,
NMR - A Window to the Human Body.

9. 2.89* BALDWIN, Prof. J.E., Oxford University,
Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis.

13. 2.89* SCHROCK, Prof. R.R., M.I.T.,
Recent Advances in Living Metathesis.

15. 2.89* BUTLER, Dr. A.R., St. Andrews University,
Cancer in Linxiam: The Chemical Dimension.

16. 2.89* AYLETT, Prof. B.J., Queen Mary College, London,
Silicon-Based Chips: The Chemists Contribution.

22. 2.89* MACDOUGAL, Dr. G., Edinburgh University,
Vibrational Spectroscopy of Model Catalytic Systems.

23. 2.89* JOHNSON, Dr. B.F.G., Cambridge University,
The Binary Carbonyls.

1. 3.89* ERRINGTON, Dr. R.J., Unniversity of Newcastle-upon-Tyne,
Polmetalate Assembly in Organic Synthesis.

9. 3.89 MARKO, DR. I., Sheffield University,
Catalytic Asymmetric Osmylation of Olefins.

14. 3.89 REVELL, Mr. P., Durham Chemistry Teachers Centre,
Implementing Broad and Balanced Science 11-16.

15. 3.89 AVEYARD, Dr. R., Hull University,
Surfactants at Your Surface.

20. 4.89 CASEY, Dr. M., University of Salford,
Sulphoxides in Stereoselective Synthesis.

27. 4.89 CRICH, Dr. D., University College London,
Some Novel Uses of Free Radicals in Organic Synthesis.

3. 5.89 ASHMAN, Mr. A., Durham Chemistry Teachers Centre,
The Chemical Aspects of the National Curriculum.

3. 5.89 PAGE, Dr. P.C.B., University of Liverpool,
Stereocontrol of Organic reactions Using
1,3-dithiane-1-oxides

10. 3.89* WELLS, Prof. P.B., Hull University,
Catalyst Characterisation and Activity.

11. 3.89 FREY, Dr. J., Southampton University,
Spectroscopy of the Reaction Path: Photodissociation Raman
Spectra of NOCl.

16. 5.89* STIBR, Dr. R., Czechoslovak Academy of Sciences,
Recent Developments in the Chemistry of Intermediate-Sited Carboranes.

17. 5.89 MOODY, Dr. C.J., Imperial College, London,
Reactive Intermediates in Heterocyclic Synthesis.

23. 5.89* PAETZOLD, Prof. P., Aachen,
Iminoboranes: Inorganic Acetylenes?

14. 6.89 JONES, Dr. M.E., Durham Chemistry Teachers' Centre,
Discussion Session on the National Curriculum.

15. 6.89 POLA, Prof. J., Czechoslovak Academy of Sciences,
Carbon Dioxide Laser Induced Chemical Reactions - New
Pathways in Gas-Phase Chemistry.

28. 6.89 JONES, Dr. M.E., Durham Chemistry Teachers' Centre,
GCSE and A Level Chemistry 1989.

11. 7.89 NICHOLLS, Dr. D.,Durham Chemistry Teachers' Centre,
Demo: "Liquid Air."

12. 9.89 CAMPBELL, Mr. W.A., Durham Chemistry Teachers' Centre,
Industrial Catalysis - Some Ideas for the National
Curriculum.

11.10.89 ASHMAN, Mr., A., Durham Chemistry Teachers' Centre,
The National Curriculum - An Update.

17.10.89* PALMER, Dr. F., Nottingham University,
Thunder and Lightning.

25.10.89* FLORIANI, Prof. C., University of Lausanne, Switzerland,
Molecular Aggregates - A Bridge Between Homogeneous and
Heterogeneous Systems.

1.11.89* BADYAL, Dr. J.P.S., Durham University,
Breakthroughs in Heterogeneous Catalysis.

9.12.89 GREENWOOD, Prof. N.N., University of Leeds,
Novel Cluster Geometries in Metalloborane Chemistry.

10.11.89	BERCAW, Prof. J.E., California Institute of Technology, Synthetic and Mechanistic Approaches to Ziegler-Natta Polymerisations of Olefins.
13.11.89	BECHER, Dr. J., Odense University, Synthesis of New Macrocyclic Systems Using Heterocyclic Building Blocks.
16.11.89*	PARKER, Dr. D., Durham University, Macrocycles, Drugs and Rock 'n' Roll.
21.11.89	JONES, Dr. M.E., Durham Chemistry Teachers' Centre, GCSE and Dual Award Science as a starting point for A Level Chemistry - How Suitable are They?
29.11.89	COLE-HAMILTON, Prof. D.J., St. Andrews University, New Polymers From Homogeneous Catalysis.
30.11.89*	HUGHES, Dr. M.N., King's College, London, A Bug's Eye View of the Periodic Table.
4.12.89	GRAHAM, Dr. D., B.P. Research Centre, How proteins Absorb to Interfaces.
6.12.89*	POWELL, Dr. R.L., ICI, The Development of CFC Replacements.
7.12.89	BUTLER, Dr. A., St. Andrews University, The Discovery of Penicillin: Facts and Fancies.
13.12.90	KLINOWSKI, Dr. J., Cambridge University, Solid State NMR Studies of Zeolite Catalysts.
15.12.89	HUISGEN, Prof. R., Universität München, Recent Mechanistic Studies of [2+2] Additions.
15.12.89	IDDON, Dr. B., University of Salford, Schools' Christmas Lecture - The Magic of Chemistry.
24. 1.90	CHADWICK, Dr. P., Dept. of Physics, Durham University, Recent Theories of the Universe (with reference to National Curriculum Attainment Target 16).
24. 1.90*	PERUTZ, Dr. R.N., York University, Plotting the Course of C-H Activations with Organometallics.
31. 1.90	DYER, Dr. U., Glaxo, Synthesis and Conformation of C-Glycosides.
1. 2.90*	HOLLOWAY, Prof. J.H., University of Leicester, Noble Gas Chemistry.

7. 2.90 THOMPSON, Dr. D.P., University of Newcastle-upon-Tyne,
The role of Nitrogen in Extending Silicate Crystal Chemistry.

8. 2.90 JOHNSON, Dr. G.A.L., Durham Chemistry Teachers' Centre,
Some Aspects of Local Geology in the National Science Curriculum (Attainment Target 9).

8. 2.90 LANCASTER, Rev. R., Kimbolton Fireworks,
Fireworks - Principles and Practice.

12. 2.90 LUNAZZI, Prof. L., University of Bologna,
Application of Dynamic NMR to the Study of Conformational Enantiomerism.

14. 2.90 SUTTON, Prof. FD., Simon Fraser University, Vancouver B.C.
Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium.

15. 2.90* CROMBIE, Prof. L., Nottingham University,
The Chemistry of Cannabis and Khat.

21. 2.90 BLEASDALE, Dr. D.C., University of Newcastle-upon-Tyne,
The mode of Action of some Anti-Tumour Agents.

22. 2.90 CLARK, Prof. D.T., ICI, Wilton,
Spatially Resolved Chemistry (Using Nature's Paradigm in the Advanced Materials Arena).

28. 2.90 RICHARDS, Mr. C., HSE, Newcastle-upon-Tyne,
Safety in School Laboratories and COSHH.

28. 2.90 THOMAS, Dr. R.K., Oxford University,
Neutron Reflectometry from Surfaces.

1. 3.90* STODDART, Dr. J.F., Sheffield University,
Molecular Lego.

8. 3.90* CHEETHAM, Prof. A.K., Oxford University,
Chemistry of Zeolite Cages.

21. 3.90 POWIS, Dr. I., Nottingham University,
Spinning Off in a Huff: Photodissociation of Methyl Iodide.

23. 3.90 BOWMAN, Pof. J.M., Emory University,
Fitting Experiment with Theory in Ar-OH.

27. 3.90 BOLLEN, Mr. F., Formerly Science Adviser, Newcastle-upon-Tyne LEA,
What's New in Satis, 16-19.

3. 7.90 JONES, Dr. M.E., Durham Chemistry Teachers' Centre,
The Chemistry A Level 1990.

9. 7.90	GERMAN, Prof. L.S., USSR Academy of Sciences, Moscow, New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes.
9. 7.90	PLATONOV, Prof. V.E., USSR Acadmy of Sciences, Novosibirsk, Polyfluoroindanes: Synthesis and Transformation.
9. 7.90	ROZHKOV, Prof. I.N., USSR Academy of Sciences, Moscow, Reactivity of Perfluoroalkyl Bromides.

* denotes lectures attended

(b) Conferences and Meetings Attended by the Author

April 1988	North East Universities and Polytechnics Graduate Symposium, Durham University.
May 1988	4th Meeting of CASE and JRS Workers on Catalysis, ICI Catalysis Research Centre, Billingham.
April 1989	RSC Faraday Discussion No. 87: Catalysis by Well Defined Materials, Liverpool.
May 1989	5th Meeting of CASE and JRS Workers on Catalysis, ICI Catalysis Research Centre, Billingham.
April 1990*	North East Universities and Polytechnics Graduate Symposium, University of Newcastle-upon-Tyne.
May 1990*	6th Meeting of CASE and JRS Workers on Catalysis, ICI Catalysis Research Centre, Billingham.

* Denotes oral presentation.