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DIRECT SYNTHESIS OF SOME SIGNIFICANT METAL ALKOXIDES

BY

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Dedication

To my three children: Regina, Maria and Samuel

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ABSTRACT

Investigations were carried out with an attempt to study direct synthesis of metal alkoxides from elemental metals and appropriate alcohols. These were done by reacting representative metals of group I, II, III & IV (which are Na, Mg, Al & Sn respectively) directly with dry ethanol and dry isopropanol. The products were then analysed by infrared spectrophotometer to identify metal alkoxides formed.

Ethanol was found to have more acidic character in reactions with these metals than isopropanol, thus its reactions with the metals were faster. Reduction in the acidic character of isopropanol, a secondary alcohol, could be due to the existence of more alkyl groups in the molecule which displays + I inductive effect.

For the same alcohol the metals reactions were found to decrease with increase in electronegativity of the metals. Sodium being the least electronegative metal reacted fastest while tin the more electronegative metal reacted slowest. Mg, Al and Sn required a catalyst, mercury (II) chloride and heat in order to initiate and drive the reactions to completion. The alkoxides formed were found to be soluble to a certain extent in the two alcohols and the order of solubility is such that Sn > Al > Mg > Na.

CHAPTER ONE

INTRODUCTION

Introduction:

Metal alkoxides are chemical substances which have been known to be excellent precursors (starting materials) for production of metal oxides[1] which are vital in electronics and ceramics industries for fabrication of electronics, glassy and ceramics materials. Their suitability resides in the ease of removal of the organic groups in the molecules and also the availability of oxygen enough to satisfy the metals requirement in forming the oxides.

Various methods for the synthesis of metal alkoxides have been studied and a lot of difficulties were met by several researchers in the attempt to achieve maximum production yield of metal alkoxides with higher degree of purity and minimum inconveniences[2]. Some of these preparatory methods are either indirect or direct ones.

The indirect methods include the use of starting materials such as metal chlorides, oxides and hydroxides; metal alkoxides (alcoholysis); and organic esters (transesterification), all of which are reacted either with alcohols or with other lower alkali metal alkoxides to yield the required metal alkoxides. These methods have several limitations.

For instance the use of chlorides with an alcohol or a lower metal alkoxide is successful with non-metal chlorides such as the chlorides of silicon and phosphorus but it is unsuccessful with less electornegative metals[2]. This is because less electronegative metal chlorides tend to solvate partially causing incomplete substitution of the chloride by the alkoxy group eventually causing formation of undesired stable complexes such as metal chloride alkoxide , heterometal alkoxides and many others (see section 2.4.3 & 2.4.4) besides the actual product which thus affect yield and purity of the desired alkoxide product.

Bradley et al[2] reacted metal oxides or hydroxides with appropriate alcohols (e,.g. ethanol) and found that the reactions tend to generate reversible reactions that produce the reactants (e.g. Section 2.4.1). This is because alkoxides are very susceptible to hydrolysis, even by atmospheric moisture. Therefore a measure has to be taken to continually remove water from the reaction mixture in order to drive the reaction to completion.

Other methods such as alcoholysis have been tried, but have also some limitations such as influence by steric factors and small difference in boiling points of the two alcohols which does not offer easy separation (see section 2.4.3.).

The direct methods involve direct reactions of elemental metals with appropriate alcohols, and have resulted in isolation of relatively high purity products (e.g. see sections 2.4.1, 2.4.3). For this reason an attempt can be made to study these direct routes in detail in order to obtain alkoxides from various metals without or with minimum formation of other undesired products.

The objectives of this research work are;

1. To study the nature of facile reactions of the selected metals: sodium, magnesium, aluminium and tin (which are representative metals of group I, II, III and IV respectively) with dry ethanol and dry isopropanol.
2. To study the effect of the size of metal atom, M, and the structure of the alkyl group, R, on the synthesis of ethoxides and isopropoxides of these metals.
3. In light of the above results to further investigate whether it could be possible to synthesize ethoxide and isopropoxide of tin by using the inorganic catalyst, mercury (II) chloride.

To fulfil these objectives the experimental approach followed consisted of:

(a) Direct reaction of representative metals of group I, II, III and IV with dry ethanol and dry isopropanol.

(b) Analysis of the products by infrared spectrophotometery.

This thesis consists of four chapters. Chapter one is the introduction followed by chapter two, the review of literature, which summarises the previous work done relevant to the research project. Chapter three contains information on the materials used in the experiments and detailed discription of experimental procedures employed to obtain the results. The last chapter, chapter four, includes results obtained from experiments carried out, discusses the findings in fair detail and ends with conclusion and recommendation.

CHAPTER TWO

LITERATURE REVIEW

2.0 Literature Review

2.1 Introduction

This literature survey contains the definition of metal alkoxides (section 2.2), discusses some aspects of the properties and chemistry of elemental metals Na, Mg. Al and Sn (Section 2.3.), reviews the preparative methods and uses of alkoxides of the metals used in this study (Section 2.4), and the general properties of metal alkoxides are presented in section 2.5.

2.2. Definition of Metal alkoxides:

Metal alkoxides, represented by a general formula $M(OR)_x$ (M = a metal of valency x; R = alkyl or aryl group) are salt like compounds containing the alkoxide ion[1], RO^-.

The alkoxide ion RO^- seems to have originated from the parent compound, alcohol ROH, in which the hydroxylic hydrogen has been replaced by a metal M. Thus metal alkoxides are basically formed by reactions of alcohols with metals. When a molecule of alkoxide containsonly one metal the alkoxide is called homometal alkoxide whereas one containing two or more different metals is called heterometal alkoxide[3].

Alkoxides can be categorized into three main groups on the basis of the parent alcohol structure. These are:-

a) normal alkoxide[4], RCH_2O^-

b) secondary alkoxide[5], R_2CHO^-

c) tertiary alkoxide[6], R_3CO^-

Metal alkoxides have been formed from various types of metals, the alkali metals; alkaline earth metals, the main-group metals; transition metals; Lanthanides; and actinides[7].

These alkoxides contain $M^{\delta+}-O^{\delta-}-C$ bonds[2] in their molecules which are polarised in the direction shown due to the highly electronegative character of oxygen. The degree of polarisation depends upon the electronegativity of the central metal M and the structure of the alkyl or aryl group R.

Metal alkoxides are known to be excellent starting materials for production of metal oxides which are vital in electronics and ceramics industries for fabrication of electronics glassy and ceramics materials[1]. Their suitability resides in the ease of removal of the organic groups in the molecules. These organic groups are easily removed in the form of volatile non-reactive products. Furthermore, because the metal is normally strongly bonded to oxygen of the alkoxide group, the metal alkoxide contains more than enough oxygen to satisfy the metals requirement in forming the oxide.

The metal oxides are produced from metal alkoxides by two important processes. These are the metal oxide chemical vapor phase deposition (MOCVD) technique and the sol-gel technique[1,3].

2.3 Metal elements and their chemistry

2.3.1 Sodium metal, Na.

Table 2.3.1.1. Some selected physical properties of sodium:

Property	Value	Reference
Atomic number	11	8
Electronic configuration	[He]---$2S^2 2p^6 3s^1$	8
Melting point/°C	97.81	8
Boiling point/°C	882.90	8
Density (20°C) gcm^{-3}	0.97	8
$\Delta H_{fus/KJ\ mol-1}$	2.60	9
$\Delta H_{vap/KJ\ mol-1}$	98	9
Pauling electronegativity	0.93	10
Specific heat/$Jg^{-1}K^{-1}$ (25^0C)	1.235	9
Ionization energy (1) KJ mol^{-1}	495	9
(2) KJ mol^{-1}	4563	9
Thermal conductivity/Jcm^{-1} S^{-1} K^{-1} (25^0C)	1.34	9
Atomic Radius (A)	1.90	8
Ionic Radius (Pauling) (A) (0.N)	0.95 (+1)	9
Standard electrode potential (volts)	-2.71	8
Covalent Radius (Pauling) (A)	1.56	9
Standard molar entropy/J/K (25^0C)	51.0S	9

Sodium metal[8] is an extremely good conductor of heat and electricity. It is less dense and in air it rapidly tarnishes, thus it is stored under oil.

Sodium occurs in rocksalt, NaCl, and Chile salt peter, $NaN0_3$. It is extracted by the electrolysis of fused sodium chloride (Downs process)[9]. Sodium belongs to the group IA metals called the alkali metals.

Because of its high reactivity it is not found in the free state in nature but exists in combination with other elements or radicals as positive ion. All group one metals adopt the body-centred cubic structure in which each atom is surrounded by .eight nearest neighbours, that is, coordination number 8 , with six more atoms only slightly further distant.

Sodium atom has one electron in the outer shell which in chemical combination is very rapidly transferred, giving a unipositive metal ion with the stable electronic configuration of a noble gas, Na^+ (2,8) is isoelectronic with Ne (2,8).

Compounds of sodium are generally predominantly ionic and exist as high melting-point solids which are white and generally water soluble.

Sodium, like other alkali metals, has low ionization energy and the single electron is so readily transferred during chemical combination because the resulting ions attract each other strongly with the liberation of energy, and therefore the overall process is highly exothermic[8].

Although the alkali metals form predominantly ionic compounds they can form covalent molecules in certain cases such as Li_2, Na_2, K_2, etc. which are found to the extent of about 1% in the vapours of these metals[10]. The bond to oxygen, nitrogen and carbon in chelate and organometallic compounds[11] also have some slightly covalent character.

Chemically sodium metal is very reactive. It reacts vigorously with water producing an alkali and hydrogen gas.

$$2Na + 2H_2O \rightarrow 2Na^+OH^- + H_2$$

Sodium reacts with a variety of non-metals when heated to give oxides, sulphides, halides and hydrides. It burns in a stream of hydrogen chloride and reacts with ammonia when heated e.g.

$$2Na + 2HCl \rightarrow 2Na^+ Cl^- + H_2$$

$$2Na + 2NH_3 \rightarrow 2Na^+NH^-_2 + H_2$$

Sodium forms the monoxide, and the peroxide $(Na^+)_2 O_2^{2-}$ if an excess of oxygen is used. The oxide ions are unstable in the presence of water in that proton from water molecule is abstracted, thus the oxide and peroxide ions function as strong bases in the Bronsted-Lowry sense[8].

e.g $(Na^+)_2 O_2^{2-} + 2H_2O \rightarrow 2Na^+OH^- + H_2O_2$

i.e $O_2^{2-} + 2H_2O \rightarrow 2OH^- + H_2O_2$

Sodium hydroxide is a white deliquescent solid which is caustic and slimy to touch. It dissolves readily in water and in alcohols with the vigorous evolution of heat. In aqueous solution it is completely dissociated and neutralises acids and displaces ammonia from ammonium salts when heated, and also reacts with many salts as well as a variety of non-metals such as the halogens, silicon and sulphur.

2.3.2. Magnesium metal, Mg.

Table 2.3.2.1 Some Selected Physical Properties of Magnesium.

Property	Value	Reference
Atomic number	12	8
Electronic configuration	[He]--- $2S^2 2P^6 3S^2$	8
Melting point/^oC	648.80	8
Boiling point/^oC	1090	8
Density $(20^oC)/gcm^{-3}$	1.74	8
$\Delta H_{fus\ KJ\ mol-1}$	9.00	9
$\Delta H_{vap\ KJ\ mol-1}$	132	9
Pauling electronegativity	1.20	12
Specific heat/$Jg^{-1}\ K^{-1}$ (25^0C)	1.030	9
Ionization energy (1) $Kjmol^{-1}$ (2) $Kj\ mol^{-1}$ (3) $Kj\ mol^{-1}$	738 1450 7730	9 9 9
Thermal conductivity /$J\ cm^{-1}\ S^{-1}\ K^{-1}$ (25^0C)	1.6	9
Atomic Radius (A)	1.61	8
Ionic Radius (Pauling) (A) (0.N)	0.65(+2)	9
Standard electrode potential (volts)	-2.37	8
Covalent Radius (Pauling) (A)	1.36	9
Standard molar entropy/J/.K (25^0C)	32.7S	9

Magnesium is a harder metal than sodium and is a good conductor of heat and electricity. On exposure to air it tarnishes to give a greyishwhite appearance. This is due to an oxide film formation that covers the silvery surface and protects it to some extent chemically[10].

Magnesium occurs as magnesite, $Mg^{2+}CO^{2-}_3$, Kieserite, $Mg^{2+}SO^{2-}_4 .H_2O$ and carnallite $KCl .MgCl_2 . 6H_2O$ and also occurs in sea water from which it is being extracted on an increasing scale. The metal is extracted by electrolysis of the fused halides[13], $Mg Cl_2$.

Magnesium is a member of group 2A metals called the alkaline earth metals. It is highly reactive and is never found in the free state in nature. It has the hexagonal close-packed structure with coordination number 12. Its atom has two electrons in the outer shell which in chemical combination are lost giving a dipositive metal ion with the stable electronic configuration of a noble gas, Mg^{2+} (2,8) is isoelectronic with Na^{+} (2,8) and Ne(2,8).

The compounds formed by Mg are therefore predominantly ionic and exist as high melting point solids. However, compounds of magnesium do show some covalent character, that is, an incomplete transfer of the two outer electrons during chemical combination. Its first ionisation energy is higher than that of sodium metal and the overall formation of ionic compound is exothermic.

Chemically magnesium is very reactive but is less so than sodium metal, for instance, it burns in steam. It is not attacked by water, despite the favorable potential, unless amalgamated[10].

At suitable temperature it combines with a variety of non-metals to give oxides, sulphides, halides and nitrides. With dilute hydrochloric acid and suphuric acid it gives the corresponding salts and hydrogen. It is attacked by most alkyl and aryl halides in ether solution to give Grignard reagents[14,15] which are employed for synthesis of alkyl and aryl compounds of other elements as well as for a host of organic synthesis.

The normal oxide $M^{2+}O^{2-}$ is formed by heating the metal in oxygen but it can conveniently be prepared by decomposition of the carbonates. Magnesium oxide is relatively inert and has a high melting point, 2800°C, and it is used for manufacturing linings for open-hearth steel urnaces.

The hydroxide is white solids insoluble in water. Like the oxide, the hydroxide is a weaker base[10]. The carbonate is only sparingly soluble in water but on heating it decomposes to give an oxide and carbon dioxide.

The chlorides, bromides and iodides are soluble but magnesium fluoride is virtually insoluble in water. The chlorides crystallise from water as hexahydrates $Mg^{2+}(Cl^-)_2 \ . \ 6H_2O$ and are very deliquescent. When heated, hydrated magnesium chloride is hydrolysed by its water of crystallisation with the evolution of hydrogen chloride and the formation of the oxide[14].

$$Mg^{2+}(Cl^-)_2 + H_2O \rightarrow Mg^{2+}O^{2-} + 2HCl$$

The bromide and iodide are appreciably soluble in organic solvents such as alcohols, ketones and esters with which they form complexes[8]. This is probably due to the formation of dative bonded complexes[8] involving bonds between the magnesium ion and the oxygen of the organic liquids.

The sulphate of magnesium occurs as Epsom salt, $Mg^{2+}SO^{2-}_4 . 7H_2O$ and is freely soluble in water thus it is the principal cause of permanent hardness in natural waters together with calcium sulphate.

2.3.3 Aluminium Metal, Al

Table 2.3.3.1 Some selected physical properties of Aluminium

Property	Value	Reference
Atomic number	13	8
Electronic configuration	[He]--- $2S^2 2P^6 3S^2 3P^1$	8
Melting point/^{0}C	660.37	8
Boiling point/^{0}C	2467	8
Density/20^{0}C) gcm^{-3}	2.70	8
$\Delta H_{\text{fus KJ mol-1}}$	10.70	9
$\Delta H_{\text{vap KJ mol-1}}$	284	9
Pauling electronegativity	1.50	12
Specific heat/Jg^{-1} K^{-1} (25^{0}C)	0.899	9
Ionization energy (1) KJ mol^{-1}	577	9
(2) KJ mol^{-1}	1816	9
(3) KJ mol^{-1}	2745	9
(4) KJ mol^{-1}	11.575	9
Thermal conductivity/J cm^{-1} S^{-1} K^{-1} (25^{0}C)	2.10	9
Atomic Radius (A)	1.43	8
Ionic Radius (Pauling) (A) (O.N.)	0.50 (+3)	9
Standard electrode potential (Volts)	-1.66	8
Covalent Radius (Pauling (A)	1.25	9
Standard molar entropy /J/K (25^0)	27.9S	9

Aluminium is a malleable, ductile metal[9] and is an excellent conductor of electricity. It is the third most abundant element in the earth's crust and is the most abundant metal. It has the hexagonal close-packed structure.

The pure form of aluminium does not occur in nature. It occurs in a variety of aluminosilicates such as clay, micas and feldspars. The only ore of it from which the metal is profitably extracted is bauxite (the hydroxo oxide), hydrated aluminium oxide, $Al_2O_3.2H_2O$. It also occurs as cryolite, Na_3AlF_6. The metal is extracted by means of electrolysis.

Aluminium is a member of group 3B metals and has three outer electrons in its atom. Because of the very large input of energy that is necessary to form the 3-valent ions (i.e. the sum of the first three ionisation energies) its compounds when anhydrous are either essentially covalent or contain an appreciable amount of covalent character.

Aluminium ion Al^{+3} is small and highly polarizing, which results in; most of its compounds being covalent; high lattice energies for ionic compounds such as the oxide and fluoride; and a high hydration energy, and therefore in a high electrode potential[8].

Chemically it is not as reactive as its high negative electrode potential would imply because normally there is a very thin oxide layer on its surface. When the surface is exposed by rubbing it with mercury, the metal reacts rapidly with moisture in the air forming aluminium hydroxide over-growths and becomes very hot in the process.

Aluminium combines directly with oxygen, sulphur, nitrogen and the halogens when heated to a sufficiently high temperature. The oxide and fluoride are essentially ionic, the rest are predominantly covalent[8].

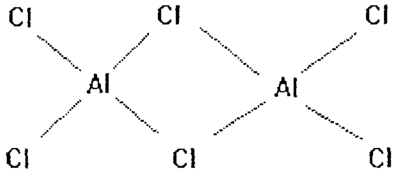
$4Al + 3O_2 \rightarrow 2(Al^{3+})_2 (O^{2-})_3$

$4Al + 6S \rightarrow 2Al_2S_3$

$2Al + 3F_2 \rightarrow 2Al^{3+} (F^-)_3$

$2Al + N_2 \rightarrow 2AlN$

The chloride exists as a dimer [16, 17]



The element aluminium, its oxide and hydroxide all are amphoteric[8, 17] The element reacts with hydrochloric acid and with strong bases as follows;

$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 3H_{2(g)}$

$2Al_{(s)} + 6NaOH_{(aq)} \rightarrow 2Na_3AlO_3\ (aq) + 3H_{2\ (g)}$

Aluminium oxide (alumina) reacts readily with dilute acids and strong alkalis to give salts;

$Al_2O_3 + 6H^+ \rightarrow \underset{\text{hydrated}}{2Al^{3+}} + 3H_2O$

$Al_2O_3 + 2OH^- + 3H_2O \rightarrow \underset{\text{Aluminate ion}}{2Al(OH)^-_4}$

The amphoteric hydroxide reacts with dilute acids and strong alkalis as follows;

$Al(OH)_{3\ (s)} + 3H^+_{(aq)} \rightarrow Al^{3+}_{(aq)} + 3H_2O_{(l)}$

$Al(OH)_{3\ (s)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4\ (aq)}$

Hydrolysis of aluminium compounds

In solution aluminium ions are thought to be hydrated by six molecules of water per ion. Because the aluminium ion is highly charged and quite small, the bond uniting the hydrogen and oxygen atoms in co-ordinated water molecules is considerably weakened, and other solvent water molecules are able to act as bases and abstract protons[8]. Hydrated aluminium ions are therefore acidic in aqueous solution.

$$[Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(H_2O)_5(OH)]^{2+} + H_3O^+$$

$$[Al(H_2O)_5(OH)]^{2+} + H_2O \rightarrow [Al(H_2O)_4(OH)_2]^{+} + H_3O^+,$$

etc.

If the solution also contains a strong basic anion such as CO_3^{2-} or S^{2-} further ionization of hydrated aluminium ions can occur.

$$[Al(H_2O)_4(OH)_2]^{+} + CO_3^{2-} \rightarrow Al(H_2O)_3(OH)_3 + HCO_3^-$$

These series of reactions show why it is impossible to obtain either aluminium carbonate or aluminium sulphide from aqueous solution. Any attempt to do so results in the precipitation of aluminium hydroxide. Aluminium forms alloys with other metals and also reduces the oxides of most other metals.

2.3.4 Tin Metal, Sn

Table 2.3.4.1 Some selected physical properties of Tin

Property	Value	Reference
Atomic number	50	8
Electronic Configuration	[He]---$4S^2 4P^6 4d^{10} 5S^2 5p^2$	8
Melting point/^{0}C	231.97(grey), 231.88(white)	8
Boiling point/^{0}C	2270(grey) , 2260 (white)	8
Density/20^{0}C) g cm^{-3}	5.75 (grey). 7.31 (white)	8
$\Delta H_{fus/KJ\ mol-1}$	7.20	9
$\Delta H_{vap\ KJ\ mol-1}$	291	9
Pauling electronegativity	1.80	12
Ioniation energy (1) KJ mol^{-1}	707	9
(2) KJ mol^{-1}	1412	9
(3) KJ mol^{-1}	2941	9
(4) KJ mol^{-1}	3929	9
(5) KJ mol^{-1}	6987	9
Thermal conductivity/J cm^{-1} S^{-1} K^{-1} (25^{0}C)	0.63	9
Atomic Radius (A)	1.51 white (1.41)	8
Ionic Radius (Pauling) (A) (0.N)	1.12 (+2); 0.71 (+ 4)	9
Standard electrode potential (Volts)	$Sn^{2+} + 2e^- \rightarrow Sn$ - 0.14 $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ + 0.15	9 9
Covalent Radius (Pauling) (A)	1.40	9
Standard molar entropy/J mol^{-1} K^{-1} (25^{0}C)	51.4S (white) 44.8S (grey)	9 9

Tin occurs as cassiterite or tinstone, SnO_2, and is the only ore of tin of any importance[8]. Its extraction[18] involves pulverising and then washing the ore with water to float away lighter impurites. Roasting is then done to remove sulphur and arsenic and is reduced to the metal by heating with anthracite, while limestone is added to produce a slag.

$$SnO_2 + 2C \rightarrow Sn + 2CO$$

Its purification or refinery is done by applying just sufficient heat to melt it; the residue usually contains iron, arsenic and lead. Tin belongs to group 4B which all exhibit a group valency of four, but because an enormous amount of energy is needed to remove four electrons from their atoms, they form compounds which are predominantly covalent. Of the group tin and lead form 2 - valent compounds in which the two s electrons are inert (inert pair effect) [8] and the 2 - valent compounds are often predominantly ionic.

Tin exhibits allotropy, three crystalline forms being known with the transition temperatures as shown below;

$$\underset{\text{grey}}{\alpha\text{ - tin}} \quad \overset{13.2^0C}{\rightleftarrows} \quad \underset{\text{white}}{\beta\text{ - tin}} \quad \overset{161^0C}{\rightleftarrows} \quad \gamma\text{-tin} \quad \overset{232^0C}{\rightleftarrows} \quad \text{liquid tin}$$

α - tin has the diamond structure whereas both β - tin and γ - tin are metallic (an approach to close packing of the atoms).

Since $\propto$ - tin has a more open structure than β - tin and γ - tin its density is considerably less than the densities of the other two allotropes. This type of allotropy in which two allotropes are equally stable at the transition temperature is referred to as enantiotropy[8].

Tin forms two oxides, tin (IV) oxide and tin (II) oxide. Tin (IV) oxide is a white solid and amphoteric, reacting with conc. sulphuric acid to give tin (IV) sulphate and with fused alkalis to give stannates (IV)

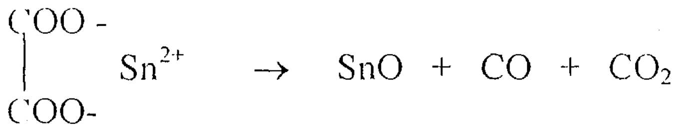
$$SnO_2 + 2H_2SO_4 \rightarrow Sn(SO_4)_2 + 2H_2O$$

$$SnO_2 + 2OH^- \rightarrow SnO_3^{2-} + H_2O$$

The stannate (IV) ion is known to be $Sn(OH)_6^{2-}$., although it is often written in the dehydrated form, SnO_3^{2-}.

Tin (IV) oxide is obtained by heating the element in oxygen or by treating it with con. HNO_3.

Tin (II) oxide, SnO, is a black solid and can be obtained by heating tin (II) oxalate (the carbon monoxide evolved provides a reducing atmosphere, preventing aerial oxidation to tin (IV) oxide).



$$\begin{array}{l}COO^-\\ |\quad Sn^{2+}\\ COO^-\end{array} \rightarrow SnO + CO + CO_2$$

It is amphoteric (more basic than tin (IV) oxide), forming tin (IV) salts with acids and stannates (IV) with alkalis (air must be excluded since stannates (II) are readily oxidised to stannate (IV)

$$SnO + 2H^+ \rightarrow Sn^{2+} + H_2O$$

$$SnO + 2OH^- \rightarrow SnO^{2-}_2 + H_2O$$

The stannate (II) ion is $Sn(OH)^{2-}_4$, but is written in the dehydrated form, SnO^{2-}_2.

Nevertheless group 4B elements are generally unstable in the presence of oxygen and water, and it is thought that intermediates are formed involving dative bonds from the attacking species to the group 4B atom (expansion of the octet). This explains why Si, Ge, Sn, and Pb can form complex anions e.g. $SnCl^{2-}_6$ $Sn(OH)^{2-}_6$ which are octahedral in shape.

2.4 Preparative Methods and Uses of alkoxides of Na, Mg, Al and Sn.

2.4.1 Sodium alkoxide:

Pure alkoxide of sodium has been prepared by dissolving the metal in alcohol at reflux temperature under an inert atmosphere of argon or nitrogen[2]. Alternatively, sodium alkoxide has been synthesized by reacting molten or amalgamated metal with small chain alcohols.

Reacting sodium hydroxide or sodium oxide with alcohols also produces sodium alkoxides according to the general equation[2, 19].

$$NaOH + ROH \rightleftharpoons NaOR + H_2O$$

$$Na_2O + 2ROH \rightleftharpoons 2NaOR + H_2O$$

The above reactions appear reversible, therefore, in order to drive the reaction to completion water formed is continually removed using organic solvents such as benzene, toluene and xylene which form azeotropes with water. The binary azeotrope could be fractionated out.

According to Bradley et al "the preparation of sodium ethoxide by this method has an additional advantage that ethanol forms a homogenous ternary azeotrope (water-ethanol-benzene) which helps in the fractionation of water very conveniently and thus good yield of the ethoxide could be achieved".

However, sodium metal is said to dissolve in alcohol and reacts with it vigorously with evolution of hydrogen gas as represented by the equation[20].

$$2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2\uparrow$$

This reaction indicates that alcohol has acid character but is weaker than that of water. The alkoxide ion being a conjugate base of an alcohol is a stronger base than hydroxide ion.

The sodium alkoxide formed is a crystalline substance soluble in alcohol. It is hygroscopic and is subject to hydrolysis by water. For example,

$$C_2H_5ONa + H_2O \rightarrow C_2H_5OH + NaOH$$

Sodium alkoxide is an important reducing agent in that it is being used in preparation of sodium derivatives of ethyl acetoacetate and ethyl malonate. Its catalytic role in organic chemistry is also seen in reaction such as Ziegler-Natta reaction of dehydrohalogenation[21].

2.4.2 Magnesium alkoxide

Magnesium metal reacts directly with alcohol with the aid of a catalyst such as iodine or mercuric chloride to produce magnesium alkoxide and hydrogen gas is evolved[22, 23].

$$Mg + ROH \xrightarrow[\text{catalyst}]{I_2 \text{ or } HgCl_2} Mg(OR)_2 + H_2\uparrow$$

According to Cerchez granular aluminium metal has to be added to the above reaction mixture to maintain the reaction in anhydrous condition so that better yield of the product is obtained. Anhydrous ethanol or isopropanol may be used.

Magnesium alkoxide is soluble in alcohol and has a catalytic role in reactions such as the direct synthesis of tetraethoxysilane from elemental silicon and anhydrous ethanol[24].

2.4.3. Aluminium alkoxide

Pure aluminium trialkoxides can be achieved by slow addition of alcohol to the metallic aluminium suspended in molten aluminium triethoxide. Similar method is employed for synthesis of aluminium triisopropoxide[25] where degreased aluminium metal is reacted with excess of isopropanol in the presence of a small amount of commercial aluminium triisopropoxide to activate the reaction. The triisopropoxide formed is distilled under reduced pressure and passes over as a colourless viscid liquid at 140°C - 150°C/12mm.

When aluminium chloride is reacted with alcohol , however, aluminium chloride undergoes only partial solvolysis[2] and subsitution. With ethanol or propanol in the presence of ether, it forms products of compositions $AlCl_3$ (OEt). $2AlCl_3.10$ EtOH and $AlCl_2$ (Opr). $2AlCl_3$. PrOH respectively.

It has been reported that the small chain alkoxy derivatives of aluminium were found to exchange their alkoxy groups with long as well as branched chain alcohols and the technique known as alcoholysis or alcohol interchange was used for the preparation of a number of new alkoxy derivatives of aluminium as shown in the general equation;

$$M(OR)_n + XR^1OH \rightleftharpoons M(OR)_{n-x}(OR^1)_x + XROH$$

However the synthetic method seems to be influenced by steric factors and difference in boiling points of the two alcohols.

Alternative to the latter method is transesterification reaction which is based on the principle that the alkoxy group of an organic ester exchanges with the alkoxy group of a metal alkoxide resulting consequently in the formation of a new alkoxide derivative of aluminium[6].

$$M(OR)_n + XCH_3\ COOR^1 \rightleftharpoons M(OR)_{n-x}\ (OR^1)_x + XCH_3COOR$$

The reaction goes to completion by fractionating out the more volatile ester produced. The method has advantages over the alcoholysis reaction in that the fractionation of more volatile ester is much easier as there is a significant difference in the boiling points of their organic esters compared with the corresponding small difference in the boiling points of two alcohols. Also the esters in some cases are much more stable than the corresponding alcohols.

Nevertheless a much easier and simpler method has been reported where aluminium metal directly reacts with alcohols in the presence of a catalyst like iodine or mercuric chloride to produce aluminium alkoxide and hydrogen gas is released[26]. e.g.

$$Al + 3\,C_2H_5OH \xrightarrow[\text{catalyst}]{I_2 \text{ or } HgCl_2} Al(OC_2H_5)_3 + 3/2H_2\uparrow$$

Aluminium alkoxides have been extensively applied in organic synthetic reactions. The ethoxide and isopropoxide reduce both aldehydes and ketones to their corresponding alcohols, a method named as "Meerwein - Ponndorf-Valey" reduction [26,27].

2.4.4 Tin alkoxide

Preparation of tin alkoxide has never been direct. Bradley et al[2, 28] reported the preparation of a number of primary, secondary and tertiary alkoxides of tin by the alcoholysis of tin tetra-isopropoxide isopropanolate with various alcohols in the presence of benzene.

$$SN(Opr^i)_4.\ Pr^iOH + 4ROH \rightarrow Sn(OR)_4 + 5pr^iOH$$

These alcoholysis reactions are comparatively faster than those of the silicon and germanium analogue and proceed to completion without any catalyst.

Another way of preparing tin alkoxide is by reacting stannic chloride with an alkali metal alkoxide such as sodium ethoxide. The reaction is said to be vigorous and exothermic yielding a yellowish tin tetraethoxide[29].

$$4NaOEt + SnCl_4 \rightarrow Sn(OEt)_4 + 4NaCl$$

This reaction is reported not to produce pure tintetraethoxide but instead produces complexes such as $Sn(OEt)_4 . 2 EtOH$, $[Sn(OEt)_6]H_2$, $[Sn(OEt)_6]HNa$, and many others. This is due to the fact that the $SnCl_4$ solvates partially and thus the chlorides are substituted partially by the ethoxy groups since tin is comparatively less active metal or less electronegative. There is therefore need to attempt to synthesize tintetraethoxide directly from tin metal and anhydrous alcohol.

2.5 General properties of metal alkoxides

The properties of metal alkoxides are determined by several factors the main ones of which are the nature of M-OR bond, the metal atomic radius and the structure of alkyl or aryl group R in the alkoxide[2].

The alkoxy derivatives of metals have the bond system $M^{\delta +} — O^{\delta -} — C$ which is polarised in the direction shown due to the highly electronegative character of oxygen (electronegativity value, 3.5 on the Pauling scale).

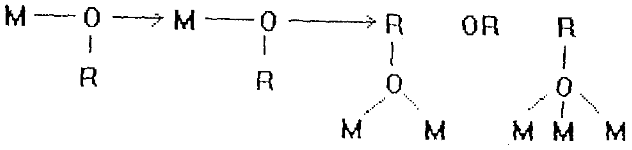
As metal alkoxides exhibit strongly polar character, metal-oxygen bonds in these derivatives are found to have around 65% ionic character for metals with electronegativity values of 1.5 - 1.3 (e.g. Al, Ti and Zr) to about 80% ionic character for metals with electronegativity values in the range of 1.2 - 0.9 (e.g. alkali metals, alkaline earths and lanthanides)[2].

The variation in the polarity of the metal-oxygen bond have been explained by two factors. These are the inductive effect (electron release) of the alkyl or aryl groups at the oxygen atom which increases with the branching of the alkyl chain and the formation of oligomers through dative bonds.

Metal alkoxides are known for their volatility, a property which is being utilized in assessing the feasibility of a metal alkoxide as a precursor in chemical vapor deposition in production of metal oxides.

Properties such as volatility and structure of metal alkoxides are governed by firstly, the structure of alkyl group. According to Bradley et al[30] volatility in alkoxides increases as the alkyl group is changed from primary to secondary to tertiary.

In primary alkoxides where the alkyl group is less branched (e.g. methyl, ethyl) volatility is low[4, 30]. This is attributed to the strong intermolecular bonding involving the central metal atom with oxygen from a neighbouring alkoxide group which gives rise to complex non-volatile alkoxide. The mechanism of these molecular association can be illustrated as



Thus primary alkoxides are mainly oligomers (dimers, trimers or tetramers) due to the bridging of the alkoxide group which may be bonded through its oxygen to two or more metals by means of conventional two-electron covalent bonds. This behaviour of metal alkoxide is enhanced by the tendency of the metal to expand its coordination number. It happens commonly with the d and f block metals.

Molecular association in tertiary alkoxides where chain branching is more is less due to steric hindrance, and also the electron releasing tendency (the + I inductive effect) makes the metal-oxygen-carbon bond less polar. For that matter most tertiary alkoxides are monomeric[1].

The second significant factor controlling volatility and structure of metal alkoxides is the metal's atomic radius. The larger the metal, the bulkier will be the alkoxide group necessary to prevent alkoxide bridging and therefore decrease in volatility.

Hydrolysis in metal alkoxide

Metal alkoxides are generally susceptible to hydrolysis[31]. To discuss hydrolysis there is need to look at the metal alkoxide bond (M - OR). In this bond ionic character exist and the positive charge exist on metal atom while the oxygen atom of the alkoxide group bears the negative charge. The bond offers sites for both nucleophilic and electrophilic attacks.

It has been suggested that hydrolysis of metal alkoxides is either acid or base catalysed. The nucleophile (OH^-) attacks the metal atom or the electrophile (H^+) attacks the oxygen. The hydrolysis results in formation of metal hydroxides which condense immediately to produce metal oxides.

Because of the tendency of some metals to expand their coordination numbers by using some of their empty d and f orbitals, complexes are sometimes formed through bonding of the metals with alkoxide ligands during hydrolysis[1, 31]. Thus a number of intermediate products, metal oxide alkoxides, are formed. The unstable ones disproportionate into the metal oxides.

CHAPTER THREE

MATERIALS AND EXPERIMENTAL PROCEDURES

3.0 Materials and experimental procedures

3.1 General Procedures:

As alkoxides in general are very susceptible to hydrolysis extra precautions were taken to eliminate any moisture that might arise from apparatus, chemicals or the atmosphere. The following measures were taken:-

3.1.1. Starting Materials:

3.1.1.1 Apparatus:

Standard quick-fit apparatus with interchangeable glass joints were used. The apparatus before each use were cleaned with chromic acid and rinsed with distilled water, then dried in an oven at a temperature of 140^0C for at least one hour. Finally the apparatus were removed and allowed to cool in a desiccator. After assemblage moisture from the atmosphere was prevented from entering the system by use of guard tube packed with calcium chloride.

3.1.1.2 Dry ethanol and isopropanol:

The absolute ethanol (boiling point 78^0C) and isopropanol (boiling point 82^0 - 83^0C) used were at the beginning those supplied by the manufacturers. Later some rectified spirit was dehydrated using calcium oxide to obtain dry ethanol[25]. Isopropanol was also dehydrated in a similar way.

3.1.1.3 Na, Mg, Al and Sn metals:

These metals were used as supplied by the manufacturers but the surfaces, where necessary, were scratched to remove some oxide film coating[20].

3.1.2 Infra-red spectra (IR):

Infrared spectrum of each prepared sample was recorded over the range 4000 - 600cm^{-1} on a Perkin - Elmer spectrometer. At each time a small amount of the sample was placed between two sodium chloride plates. For solid samples each was ground in an agate mortar and mixed with sufficient amount of nujol to make a lighter paste as desired for spotting between sodium chloride plates[32].

3.2 Reactions Procedures:

The experiments have been divided into two parts. Firstly the direct reactions of each of the metals Na, Mg, Al and Sn with absolute ethanol and secondly the direct reactions of each of the mentioned metals with dry isopropanol. The resulting products are all analysed using infrared spectrophotometer.

3.2.1 Reaction between Sodium metal and absolute ethanol:

Procedure:

2.4g of freshly cut sodium metal was carefully weighed and placed in a 50ml beaker containing paraffin. It was then cut into smaller pieces.

A system consisting of 100ml quick-fit flask fitted with a reflux condenser and a guard tube containing calcium chloride was assembled in a hood. 50ml of absolute ethanol was transferred into the flask. Using a pair of long tweezers the pieces of sodium metal were rapidly added to the ethanol, one piece at a time. A vigorous reaction occurred accompanied by evolution of hydrogen gas and heat.

At the end of the reaction the content of the flask was refluxed at 80^0C for three hours with continous stirring to ensure complete reaction of sodium. The resultant reaction mixture was distilled to remove excess ethanol leaving behind a thick white solid product which quickly turned brown . The product was about 89% yield and was then analysed by using IR spectrophotometer. (See figure 4.1.1.1).

3.2.2 Reaction of Magnesium metal with absolute ethanol.

Magnesium ribbon was first cleaned by scratching off some oxide film coated on its surface using razor blade.

3g of the cleaned magnesium ribbon were cut into smaller pieces and were added to a 250ml quick-fit flask containing 180ml absolute ethanol. The same apparatus setup as in the previous experiment was used.

No reaction occurred at room temperature. The content of the flask was heated for some time to possibly initiate a reaction. The mixture was then refluxed for about thirty hours. On cooling, the reaction mixture was filtered to separate magnesium metal and the filtrate was distilled to remove excess ethanol.

However, all the ethanol used was recovered and there was no trace of anything like product left at the bottom of the flask. This indicated that no product was formed and therefore no reaction occurred.

3.2.3 Reaction of Magnesium metal with absolute ethanol using mercury (II) chloride as catalyst.

The previous experiment was repeated using a catalyst, mercury (II) Chloride. 3g of clean pieces of magnesium ribbon were transferred to a 250ml flask containing 180ml absolute ethanol. On addition of small quantity of mercury (II) chloride to the mixture in the flask no reaction was seen at room temperature.

The content of the flask was then heated and refluxed for about 18 hours with constant stirring using magnetic stirrer. Some white crystals appeared on the bottom of the flask. Remain of pieces of magnesium ribbon which appeared crumbled and perforated, plus some blackish solid substances were filtered off and the filtrate was distilled at 78^0C to remove excess ethanol.

A portion of the concentrated solution was removed for IR analysis (see figure 4.2.1.1.) and the remaining solution was heated to dryness. Small quantity of white crystals was obtained as product, about 20% yield.

3.2.4 Reaction between Aluminium metal and absolute ethanol using mercury (II) Chloride catalyst:

3g of cleaned aluminium foil were placed into a 3-necked quick fit flask containing 180ml dry ethanol. A very small amount of mercury (II) chloride was added to the mixture as catalyst. A thermometer and a condenser protected with guard tube containing calcium chloride were inserted on two necks of the flask[25].

At room temperature there was no reaction but was initiated by heating the mixture for some few minutes. When heating was stopped a vigorous reaction erupted releasing free hydrogen gas as it progressed but later the rate gradually slowed down.

The reaction mixture was then refluxed for 18 hours at 80^0C with constant stirring using magnetic stirrer. Unreacted aluminium together with other solid residue were removed by filtration leaving solution of the product as filtrate. The solution was distilled at 80^0C at normal atmospheric pressure to remove excess ethanol and white gelatinous crystals were obtained as product, about 18.7% yield and was analysed by IR spectrophotometer (See figure 4.3.1.1.)

3.2.5 Reaction between Tin metal and dry ethanol using mercury (II) chloride catalyst.

3g of cleaned pieces of tin foil were placed into a 250ml quick-fit flask containing 150ml dry ethanol. A small amount of mercury (II) chloride was added into the mixture. At room temperature there was no observable reaction.

The content of the flask was heated and refluxed for about 15 hours at 80^0C with continuous stirring. The reaction mixture then turned pale yellow. No crystals were seen.

A very small amount of mercury (II) chloride was added again together with some little ethanol, (30ml), and refluxing was continued for another 15 hours. At this stage the pale yellow colour deepened and the mixture was allowed to stand for 24 hours. It was then filtered to remove unreacted tin foil and other residue present.

The yellowish filtrate was distilled under reduced pressure to remove unreacted ethanol and yellowish crystals were obtained about 17.6% yield and the IR analysis was done (See figure4.4.1.1.)

3.2.6 Reaction between sodium metal and dry isopropanol:

2.4g of freshly cut sodium metal were carefully added, a small piece at a time, to a 250ml flask containing 50ml dry isopropanol. The flask carried a condenser at the end of which was fixed a guard tube thermometer.

A reaction less vigorous than reaction 3.2.1 occured with liberation of hydrogen gas and heat. When it was accelerated by heating and then refluxed for 2 hours a thick mass of white crystals were formed that consumed almost all the isopropanol.

Another 50ml of dry isopropanol was added to the mixture and with constant stirring it was refluxed at 82^0C for an additional two hours to drive the reaction to completion. A light brown solution was formed and was distilled at 82^0C to remove unreacted isopropanol. A large amount of crystals (mixture of white and brown colour) were obtained , about 85% yield and was analysed by IR spectrophotometer (See figure 4.5.1.1).

3.2.7 Reaction between Magnesium metal and dry isopropanol using mercury (II) chloride catalyst.

3g of cleaned pieces of magnesium ribbon and 180ml dry isopropanol were put into a 250ml quick-fit flask. A very small amount of mercury (II) chloride was added as catalyst. The content of the flask was heated to initiate the reaction which was otherwise inert at room temperature. and was refluxed for eighteen hours at 82^0C with continuous stirring.

The mixture was then filtered to remove unreacted magnesium metal which in appearance is neither crumbled nor perforated. The filtrate was distilled to remove excess isopropanol . Some concentrated solution of the product was taken for IR analysis and the remainder was heated to dryness. A very small amount of white crystals was obtained far smaller than product of experiment 3.2.3, yield 10.7% , and the' IR analysis was carried out(See figure 4.6.1.1).

3.2.8 Reaction between Aluminium metal and dry isopropanol using mercury (II) Chloride catalyst.

3g of aluminium foil were placed into a 250ml quick-fit flask containing 180ml dry isopropanol and a tiny amount of mercury (II) chloride catalyst was added. The reaction was initiated by heating the mixture for sometime. When heating was stopped a vigorous reaction started which continued until it slowed down. Thereafter the mixture was refluxed for about 18 hours with continuous stirring[25].

The reaction mixture was filtered to remove unreacted aluminium together with other black solid substances formed during the reaction process. The filtrate was distilled at 82^0C to remove unreacted isopropanol and a small quantity of white crystals were obtained , yield about 15.2% and analysed by IR spectrophotometer (See fiure 4.7.1.1).

3.2.9 Reaction between Tin metal and dry isopropanol using mercury (II) chloride catalyst.

3g of cleaned tin foil was transferred into a 250ml quick-fit flask containing 150ml dry isopropanol and a small amount of mercury (II) chloride catalyst was added. The mixture was heated to start the reaction and when it was refluxed for 15 hours a light pale yellowish colouration appeared.

A tiny quantity of mercury (II) chloride catalyst was added again together with 30ml dry isopropanol and the refluxing was resumed and extended for another 15 hours with effective stirring of the reaction mixture. The reaction, however, appeared slower than reaction 3.2.5. The reaction mixture was left to stand for 24 hours.

Filtration was carried out to remove unreacted tin foil from solution of the product and the solution was distilled to remove excess isopropanol. A very small amout of yellowish crystals was obtained but was found to be smaller than the product of experiment 3.25, yield about 12.4% , and the IR analysis of the product was carried out (See figure 4.8.1.1.).

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.0 Results and Discussions

4.1 Preparation of Sodium ethoxide:

Cleaned sodium metal and absolute ethanol were used. The reaction was vigorous and exothermic according to the following equation.

$$2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2\uparrow$$

Sodium metal was added a piece at a time to prevent excessive production of heat. The reaction mixture was refluxed at 80^0 C for three hours with effective stirring to achieve complete reaction of sodium metal and to prevent decomposition of ethoxide at high temperature.

On removal of excess ethanol by distillation the resultant product was white crystals of sodium ethoxide, about 89% yield, and is sparingly soluble in ethanol. The colour of the solid product quickly turned brown on contact with outside air. This could be attributed to oxidation of it in air. The infrared spectrum of the product is shown in figure 4.1.1.1.

4.1.1 Infrared analysis of the product

TABLE 4.1.1.1 Infrared spectral analysis of the product obtained from the reaction between sodium metal and dry ethanol

Frequency cm^{-1} and intensity*	Assignment
3300b	OH stretch
2970s 2920w 2860 m	C - H stretch (asymmetric & Symmetric) of - CH_2 - CH_3
1440 s 1375 s	C - H Bend in CH_3
1100 s 1050 vs	C - O stretch
880 s 800 vw	CH_2 - CH_3 Bend

*** b - broad s - strong vs - very strong w - weak m - moderate**

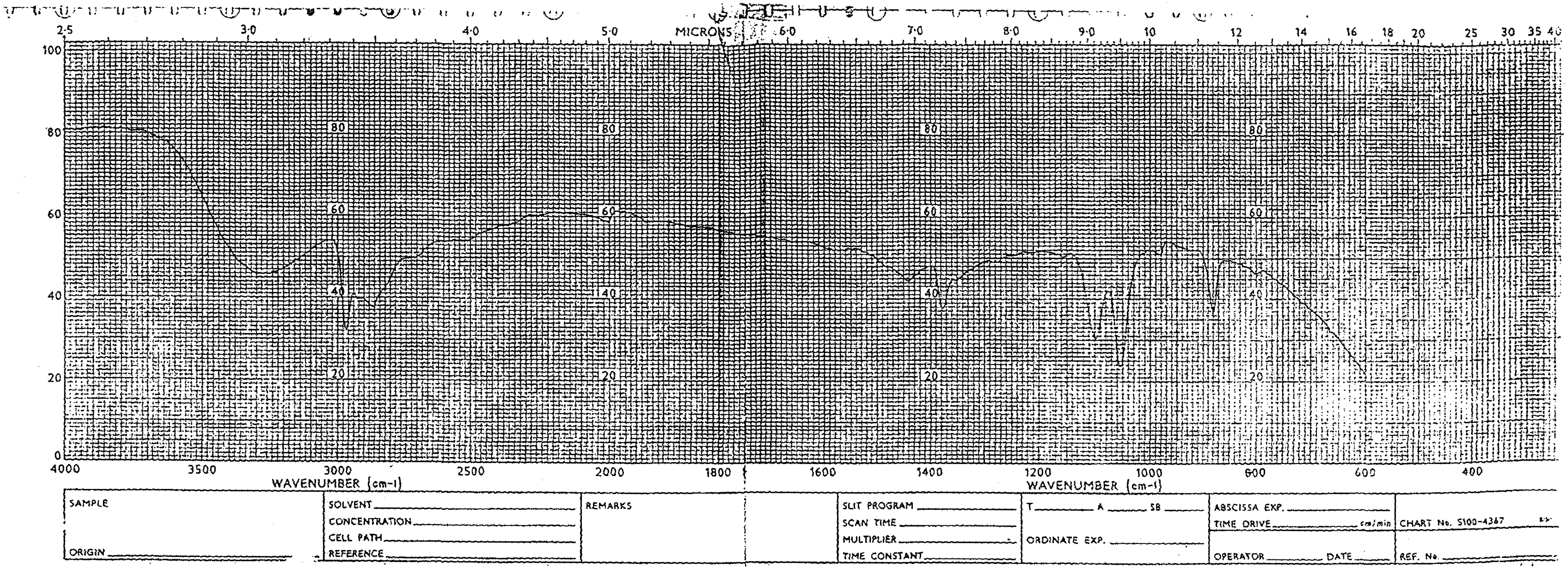


Fig. 4.1.1.1 Infrared spectrum of the product obtained from the reaction between sodium metal and dry ethanol.

4.2 Preparation of Magnesium diethoxide:

The reaction required cleaned pieces of magnesium ribbon and absolute ethanol. The mixture at the beginning did not yield any product even when refluxed for about 30 hours. This was revealed when all ethanol used was recovered on distillation of the reaction mixture and there was no trace of crystals left at the bottom of the flask.

When the same amount of fresh reactants was mixed with tiny amount of mercury (II) chloride catalyst and then heated and refluxed for about 18 hours some white crystals appeared at the bottom of the flask. Removal of unreacted pieces of magnesium ribbon together with some black solid substances by filtration left a filtrate which on distillation at 78^0C removed unreacted ethanol. Small amount of white crystals of magnesium diethoxide was obtained in 20% yield .

$$Mg + 2C_2H_5OH \xrightarrow[\text{Heat}]{HgCl_2\ \text{Catalyst}} Mg(C_2H_5O)_2 + H_2\uparrow$$

The lower yield could indicate that some magnesium oxide and hydroxide might have been formed during the reaction process.The product was found to be soluble in ethanol and this solubility could be linked with the fact that compounds of magnesium sometimes possess some covalent character. The infrared spectrum of the concentrated solution is shown in figure 4.2.1.1.

4.2.1 Infrared analysis of the product.

TABLE 4. 2.1.1 Infrared spectral analysis of the product obtained from the reaction between magnesium metal and dry ethanol

Frequency Cm^{-1} and intensity	Assignment
3350 b	OH stretch
2960 s 2920 w 2880 m	C - H (asymmetric & Symmetric) stretch
1450 - 1250	C - H bend
1075 s 1035 vs	C - O stretch
875 vw	CH_3 - CH_2 Bend

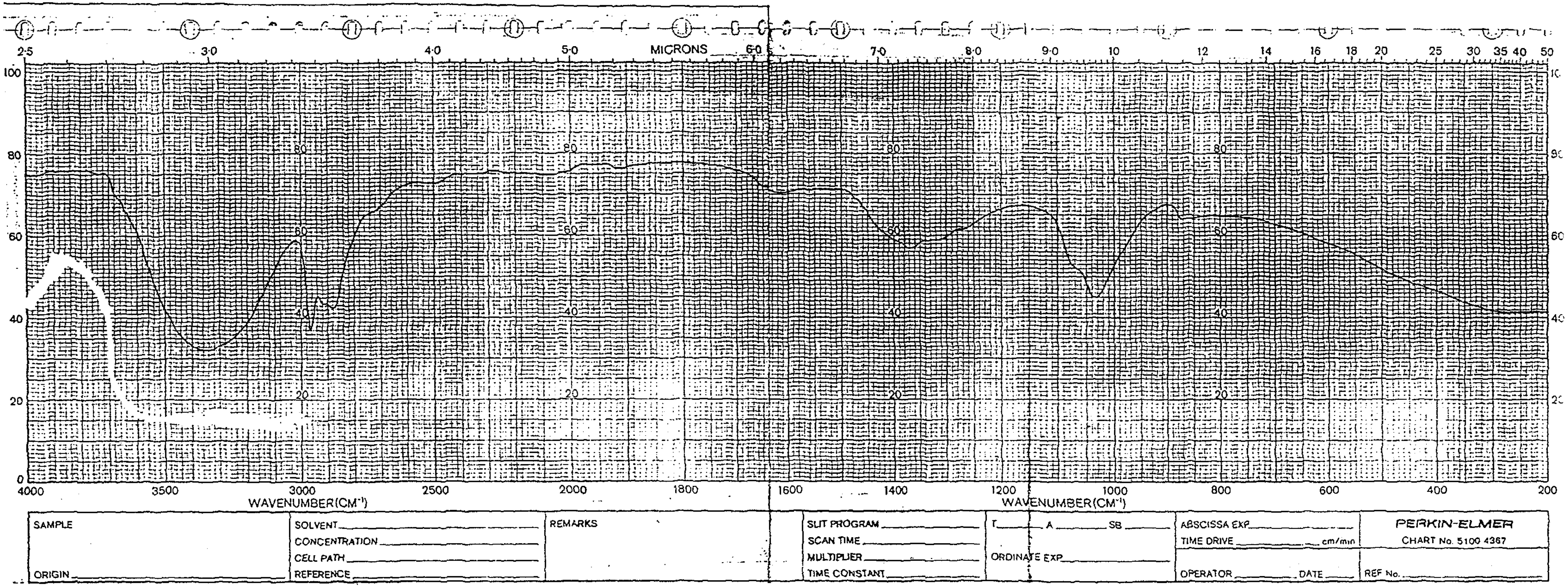


Fig. 4.2.1.1 Infrared spectrum of the product obtained from the reaction between magnesium metal and dry ethanol.

4.3 Preparation of aluminium triethoxide:

The reactants were aluminium foil and dry ethanol with small amount of mercury (II) chloride as catalyst. The reaction was accelerated by heating the mixture for few hours. When heating was stopped a vigorous reaction started with evolution of hydrogen gas. When the reaction rate slowed down the reaction mixture was then refluxed at 80^0C for 18 hours.

$$Al + 3C_2H_5OH \xrightarrow[\text{Heat}]{HgCl_2 \text{ Catalyst}} Al(C_2H_5O)_3 + 3/2\,H_2\uparrow$$

Unreacted aluminium was filtered off and the filtrate was distilled at a temperature of 80^0C at normal atmospheric pressure to eliminate excess ethanol. A good quantity of white gelatinous solid was obtained, yield about 18.7 %, and the infrared spectrum was produced as shown in figure 4.3.1.1.

4.3.1 Infrared analysis of the product

TABLE 4.3.1.1 Infrared spectral analysis of the product obtained from the reaction between aluminium and dry ethanol

Frequency Cm^{-1} and intensity	Assignment
3350 b	OH stretch
2970 s 2920 w 2880 m 1925 w	C - H stretch (Asymmetric and Symmetric)
1630 w 1450 m 1375 s 1270w	C - H Bend
1080s 1040vs	C - 0 stretch
875 m	Al - 0 - Al Asymmetric stretch

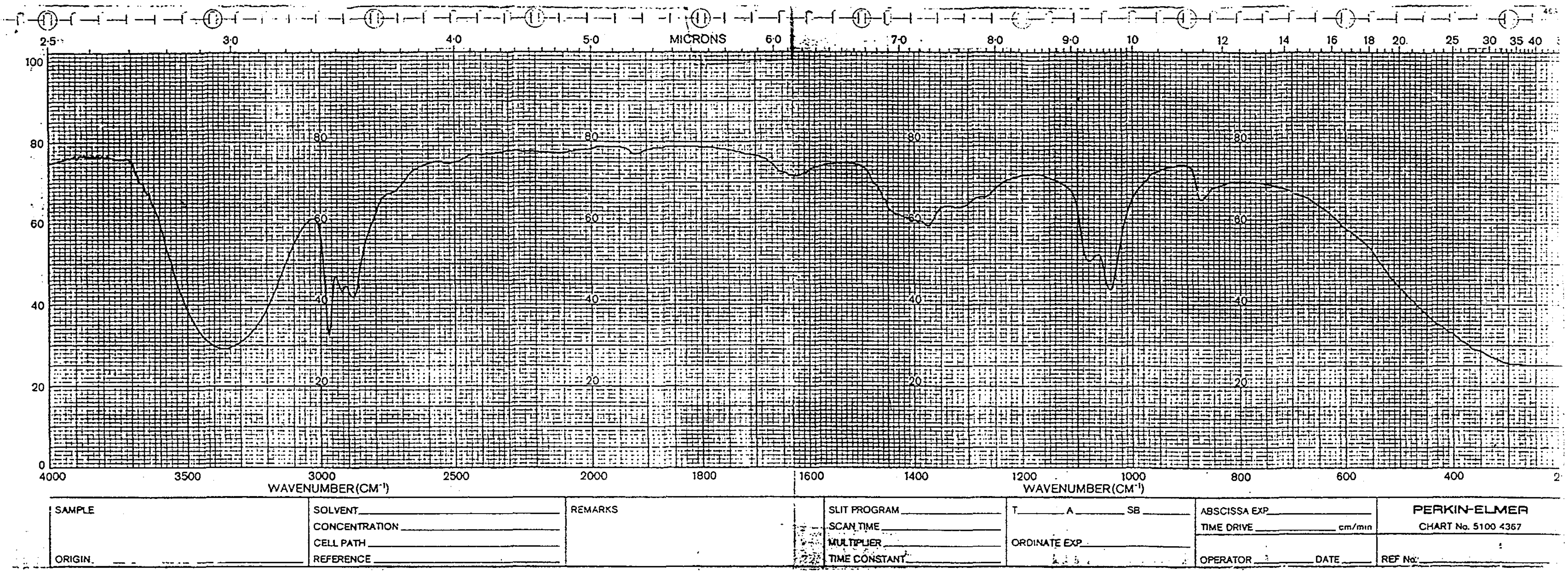


Fig. 4.3.1.1. Infrared spectrum of the product obtained from the reaction between aluminium metal and dry ethanol.

4.4 Preparation of Tintetraethoxide:

Cleaned pieces of tin foil were reacted with dry ethanol, catalysed by mercury (II) chloride. The reaction was initiated by heating and the mixture was refluxed with continuous stirring for 30 hours at 80^0C. The reaction mixture assumed pale yellow colour which deepened as the reaction progressed.

$$Sn + 4C_2H_5OH \xrightarrow[\text{Heat}]{HgCl_2 \text{ Catalyst}} Sn\ (OC_2H_5)_4 + 2H_2\uparrow$$

After elimination of unreacted tin foil and residue by filtration the yellowish filtrate was distilled to eliminate excess ethanol and some yellowish crystals of tintetraethoxide were obtained, about 17.6% yield. . The infrared Spectrum is shown in figure 4.4.1.1.

4.4.1 Infrared analysis of the product

TABLE 4.4.1.1 Infrared spectral analysis of the product obtained from the reaction between tin metal and dry ethanol

Frequency Cm^{-1} and intensity	Assignment
3340 b	OH stretch
2950 s 2920 vs 2850 s	C - H (asymmetric & Symmetric) stretch
1600 m 1455 vs 1375 s 1250 w	C - H Bend
1085 m 1025 s	C - O stretch
880 m	Sn - O Asymmetric strech

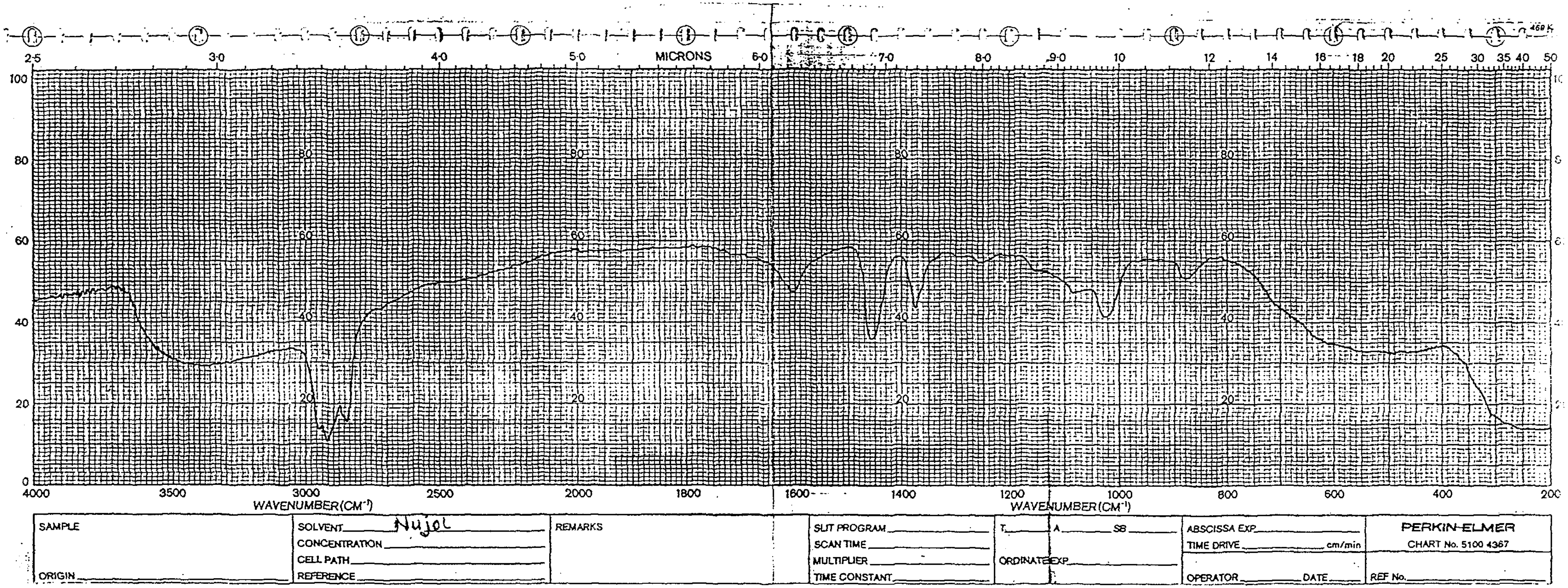


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Fig. 4.4.1.1. Infrared spectrum of the product obtained from the reaction between tin metal and dry ethanol.

4.5 Preparation of sodium isopropoxide:

The reaction procedure used here was the same as that of experiment 3.2.1. The same quantity of cleaned sodium metal was reacted with 100ml dry isopropanol instead of dry ethanol. The reaction was relatively slow and moderate and hydrogen gas was evolved gently with little production of heat.

$$2Na + 2C_3H^i_7OH \rightarrow 2NaOC_3H^i_7 + H_2\uparrow$$

The reaction was completed by heating and the mixture was refluxed with continous stirring for a total of four hours. A light brown solution was formed which on distillation at 80^0C expelled excess isopropanol and light brown crystals were obtained as product, yield about 85%, and the infrared spectrum was produced as shown in figure 4.5.1.1. Sodium isopropoxide formed was observed to oxidize less rapidly than sodium ethoxide.

4.5.1 Infrared analysis of the product

TABLE 4.5.1.1 Infrared spectral analysis of the product obtained from the reaction between sodium and dry isopropanol

Frequency Cm^{-1} & Intensity	Assignment
3700 b	OH stretch
3200 s	C - H (asymmetric &Symmetric) stretch
1650 m	C - H Bend and Gem dimethyl group
1525 s	
1450 s	
1370 m	
1200 s	
1175 s	C- 0 stretch
990 s	
850 w	
740 vw	- CH_3 - CH_2 Deformation

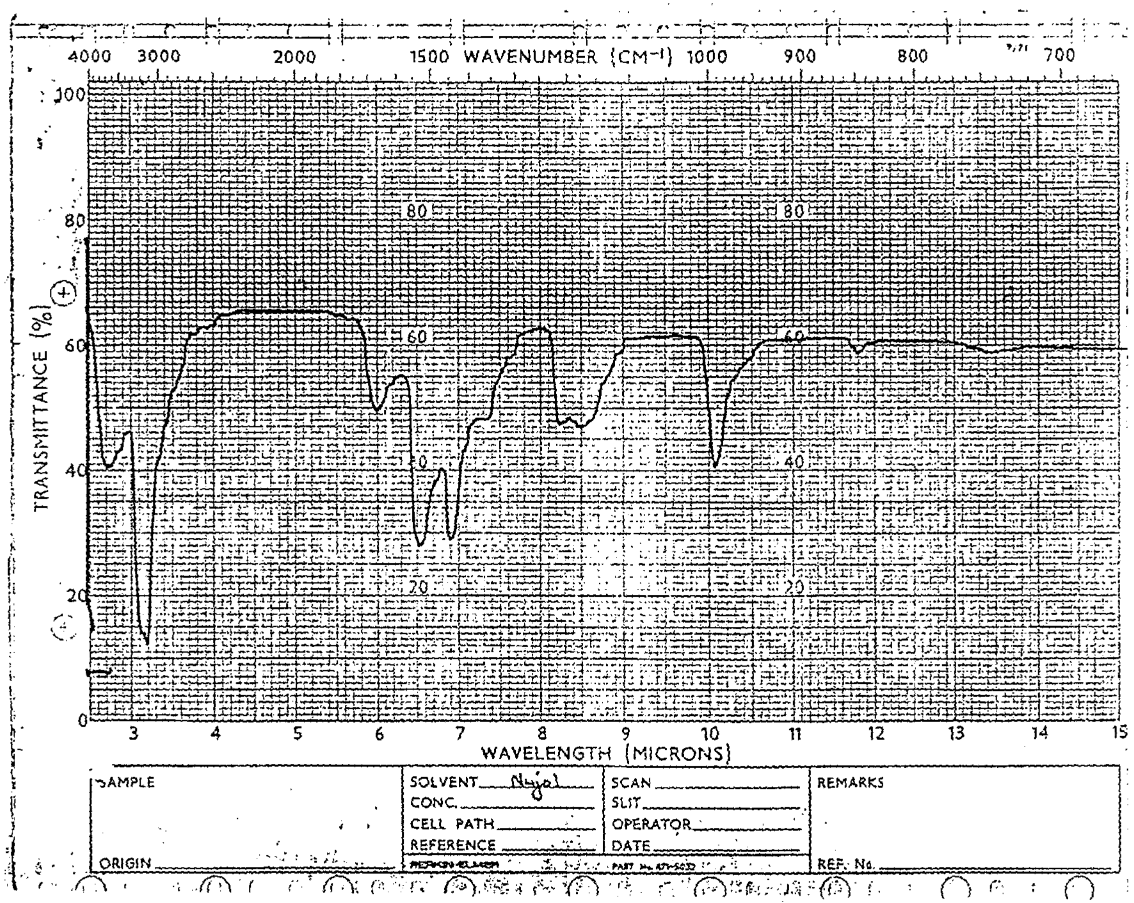

Fig. 4.5.1.1. Infrared spectrum of the product obtained from the reaction between sodium and dry isopropanol.

4.6 Preparation of magnesium diisopropoxide

Pieces of cleaned magnesium ribbon were reacted with dry isopropanol. The same amount of these reactants were used as in experiment 3.2.3 and catalysed by mercury (II) chloride. The inert reaction at room temperature was initiated by heating and the reaction mixture was refluxed for 18 hours at 82^0C under normal atmospheric pressure. Hydrogen gas was released according to the equation.

$$Mg + 2C_3H^i_7OH \xrightarrow[\text{Heat}]{HgCl_2\ \text{Catalyst}} Mg\ (i\text{-}OC_3H_7)_2 + H_2 \uparrow$$

Unreacted pieces of magnesium were removed by filtration and the filtrate was concentrated by removal of excess isopropanol by distillation. A sample of it was taken for infrared analysis (see figure 4.6.1.1.) and the remaining concentrated solution of magnesium diisopropoxide was carefully heated to dryness. A very small amount of white crystals was obtained, yield about 10.7%, but was found to be smaller than the product of experiment 3.2.3.

4.6.1 Infrared analysis of the product

TABLE 4.6.1.1 Infrared spectral analysis of the product obtained from the reaction between magnesium and dry isopropanol

Frequency Cm^{-1} and intensity	Assignment
3360 b	OH stretch
2970 s 2920 m 2880 m 2700 w 2650 w	C - H stretch (asymmetric and Symmetric)
1455 m 1370 s 1300 m	C - H Bend and Gem . dimethyl group
1150 s 1125 s 945 s	C - O stretch
820 w	CH_3 - CH_2 Deformation

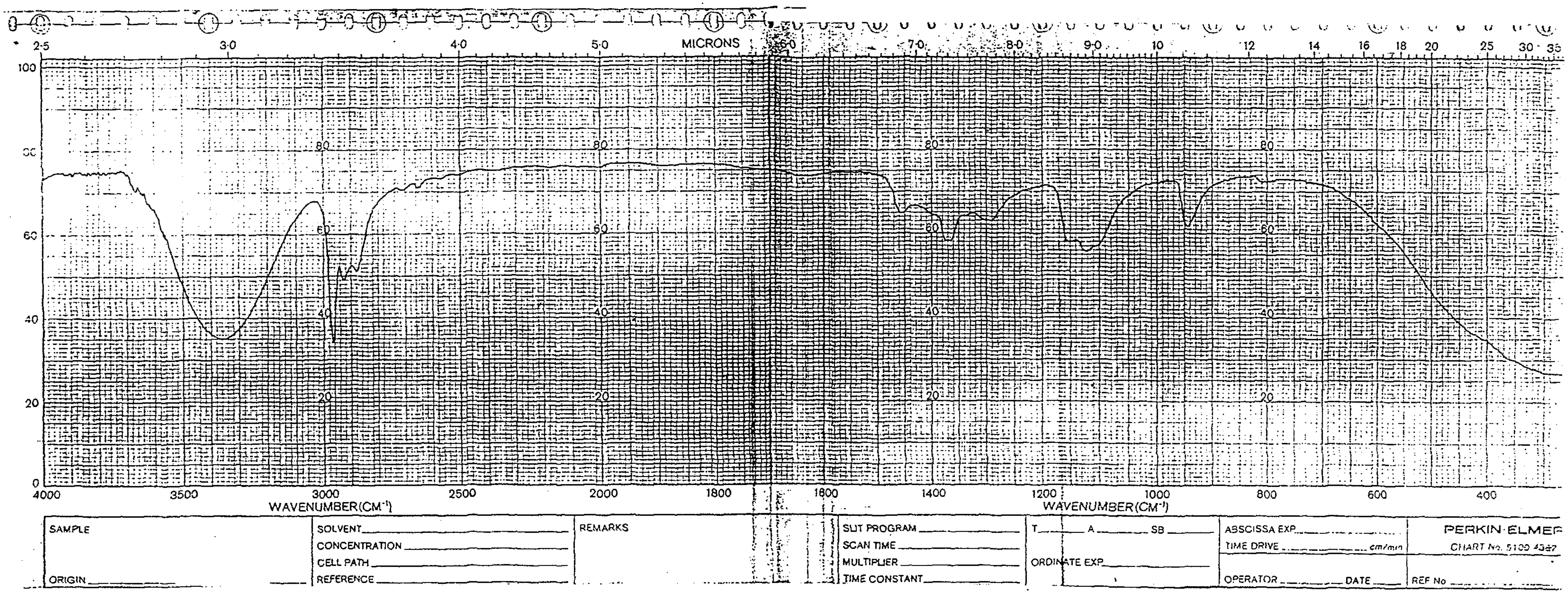

Fig. 4.6.1.1. Infrared spectrum of the product obtained from the reaction between magnesium metal and dry isopropanol.

4.7 Preparation of aluminium triisopropoxide

The raw materials were aluminium foil and 180ml dry isopropanol, and mercury (II) chloride was used as catalyst. On initiating the reaction by heating the mixture for sometime a vigorous evolution of hydrogen gas was sparked off. When heating was stopped the evolution of gas continued for a while and later ceased.

At this stage the reaction mixture was then refluxed at 82^0C for 18 hours accompanied by continuous stirring. Some white crystals appeared at the bottom of the flask.

$$Al + 3C_3H^{i}_7OH \xrightarrow[\text{Heat}]{HgCl_2\ \text{Catalyst}} Al\ (i - OC_3H_7)_3 + 3/2\ H_2 \uparrow$$

Unreacted aluminium and other black residual substances were removed by filtration leaving clear filtrate which was concentrated by distilling off excess isopropanol and was then carefully heated to dryness to secure some white gelatinous crystals, yield about 15.2%. Its infrared spectrum is shown in figure 4.7.1.1.

4.7.1 Infrared analysis of the product

TABLE 4.7.1.1 Infrared spectral analysis of the product obtained from the reaction between aluminium and dry isopropanol

Frequency Cm^{-1} and intensity	Assignment
3350 b	OH stretch
2920 vs 2850 vs 2720 w 2620 w	C - H stretch (asymmetric and Symmetric)
1455 vs 1375vs	C - H Bend and Gemdimethyl group
1165 vs 1120 vs 1030 s	C - O stretch
945 vs 830 s 670 s 600 w	Al - 0 - Al (asymmetric and Symmetric) stretch

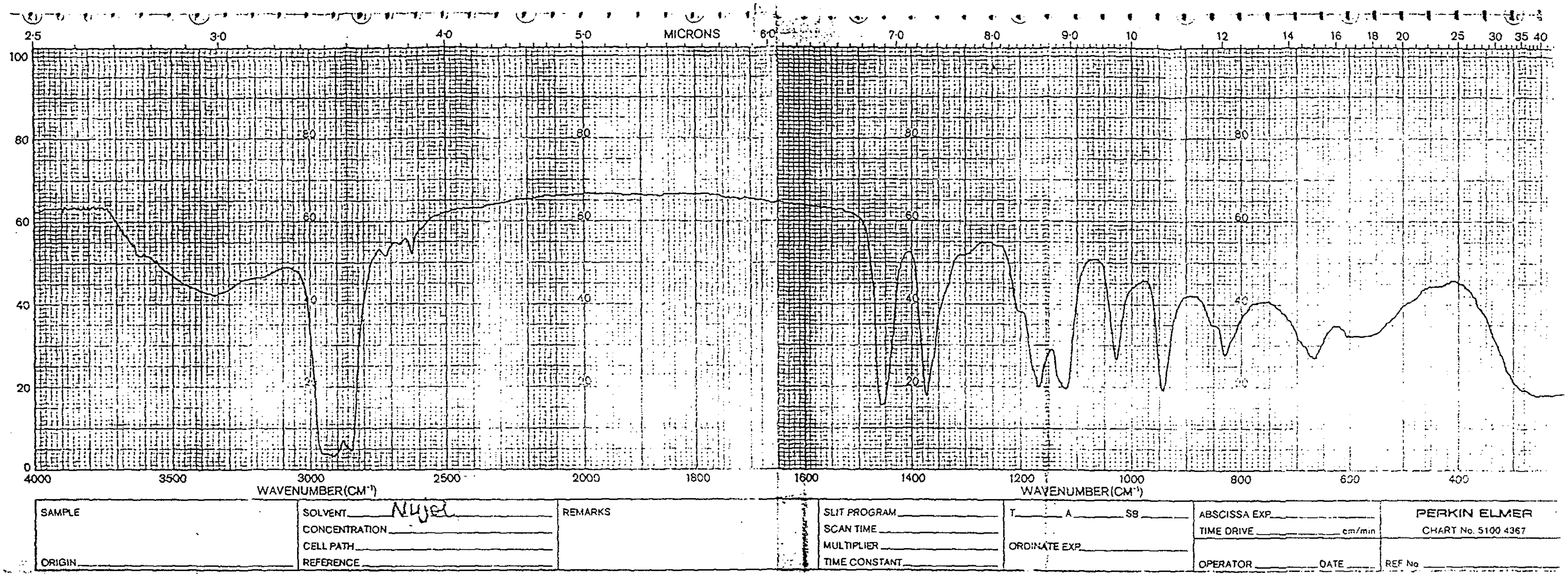

Fig. 4.7.1.1. Infrared spectrum of the product obtained from the reaction between aluminium metal and dry isopropanol.

4.8 Preparation of tintetraisopropoxide

The reactants were cleaned tin foil and dry isopropanol all of the same quantity as the reactants of experiment 3.2.5 and catalysed by mercury (II) chloride. When the reaction was initiated by heating and refluxed for 30 hours a pale yellow mixture was produced. However the reaction was slower than reaciton 3.2.5.

$$Sn + 4C_3H^{i}_7OH \xrightarrow[\text{Heat}]{HgCl_2\ \text{Catalyst}} Sn\ (i - OC_3H_7)_4 + 2H_2\uparrow$$

Unreacted tin foil was filtered off and the pale yellow filtrate was distilled to eliminate unreacted isopropanol and very tiny yellowish crystals of tin tetraisopropoxide were formed, yield about 12.4% , and was analysed by infrared spectrophotometry as shown in figure 4.8.1.1.

4.8.1 Infrared analysis of the product

TABLE 4.8.1.1 Infrared spectra of the product obtained from the reaction between tin metal and isopropanol

Frequency Cm^{-1} and intensity	Assignment
3400 b	OH stretch
2960 vs 2920 vs 2850 vs	C - H stretch (asymmetric and symmetric)
1700 w 1600 m 1530 m 1450 s 1400 m 1375 m 1255 vs	C - H Bend and Gemdimethyl group
1100 - 1000 bs	C - O stretch
850 m 790 s	Sn - O stretch
650 - 500 bw	Sn - C stretch

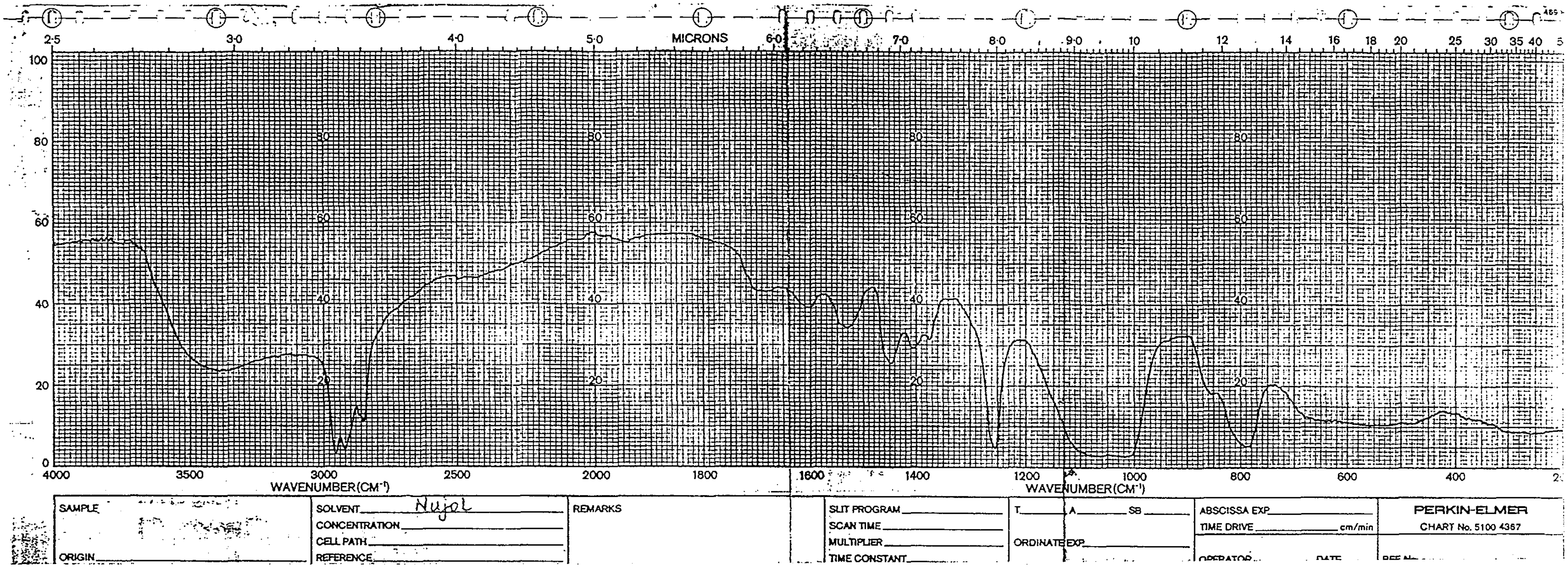

Fig. 4.8.1.1. Infrared spectrum of the product obtained from the reaction between tin metal and dry isopropanol.

4.9 Infrared Spectral Analysis of all the products

Although infrared technique has not often been definitive in structural assignments it has been utlized to support the identity of metal alkoxides by observing bands characteristic of the bonded alkoxide group such as M - O and C - O stretching vibrations[2].

The infrared spectra of the products obtained in experiment 3.2.1 - 3.2.9 have been shown in figures 4.1.1.1 to 4.8.1.1 and their analysis are shown in tables 4.1.1.1 to 4.8.1.1 respectively. The assigned frequencies closely agreed with the reported literature values[2, 32, 33].

All the infrared spectra have indicated the existence of H-bonding[34] (i.e. intermolecular hydrogen bonding) as shown by the broad - OH stretch around 3400cm^{-1}. Not H-bonded OH stretch appears at 3600cm^{-1}. This is an indication of the hygroscopic nature of alkoxides which might have occurred during filtration of reaction mixture after reflux, resulting in possible formation of some metal hydroxide (see section2.3.1). The strong bands due to M-O-C in the ethoxides in the range 1000 - 1100cm^{-1} are indicative of primary alkoxides. The peaks between 2860-2970cm^{-1} are the C - H asymmetric and symmetric stretches due to $-CH_2$ and $-CH_3$ in the ethoxides as well as in the isopropoxides and those below 1000cm^{-1} could be either of $-CH_2$ and $-CH_3$ internal deformation in ethanol molecules indicating that a product is not absolutely alcohol free or could be vibrations of M - O twisting and rocking type.

In the isopropoxides the M - O - C bands appear in the range 950 - 1175cm^{-1} indicative of secondary alkoxides while the M - O twisting and rocking type appear below 950cm^{-1} and are so clearly identified in aluminium and tin isopropoxides[2]. These isopropoxides exhibit a strong doublet at about 1375cm^{-1} and 1365cm^{-1} due to geminal dimethyl groups[2, 35].

The M - O stretching modes in aluminium and tin isopropoxides have occurred at several frequencies more than in ethoxides . This could be due to the twisting and rocking mode of molecular behaviour. This is because Al and Sn undergo covalency expansion by intermolecular coordination through the oxygen atom of the alkyl group and is supported by the fact that covalent character of the M - O bond increases with greater + I inductive effect of the alkyl group. Metal oxide formation at lower scale from these alkoxides may take place by oxidation in air during drying of the solid products, and could account for the lower yield of these ethoxides and isopropoxides.

The determination of oligomerism of these ethoxides and isopropoxides could only be made possible by carrying out NMR analysis. However, the solid state and insolubility of many of these alkoxides in the alcohols could be attributed to their being ionic and polymeric.

4.10 General discussion

By simple observation the ease of the reactions of these selected metals with ethanol and isopropanol seem to decrease with the increase in electronegativity of the metals. That is to say the order of ease of reaction is Na > Mg > Al > Sn (with electronegativity values of 0.93, 1.20, 1.50, 1.80, respectively) for the same alcohol. This is supported by the fact that while sodium reacted readily with the two alcohols, magnesium, aluminium and tin reacted only in the presence of the catalyst mercury (II) chloride, and in addition heat was required to initiate the reactions in order to produce observable products.

The reactions also seem to be influenced by the type of alcohol. For the same metal the reaction with ethanol was faster than with isopropanol. This has been revealed by comparing the time taken in each reaction and the amount of product obtained. This effect reflects the fact that ethanol is more acidic than isopropanol. The lower acidity of isopropanol may be due to the (+ I) inductive effect of the alkyl group.

It was also observed that in the synthesis of magnesium and aluminium ethoxides and isopropoxides some tiny crystals of these alkoxides appeared during the refluxing stage but the bulk were in solution form in the alcohols. Their solubility could be attributed to the fact that magnesium and aluminium possess some metallic and non-metallic properties and therefore the alkoxides can also display some covalent characteristics. However, tin ethoxide and isopropoxide have shown greater solubility in the corresponding alcohols. During the refluxing of the reaction mixtures crystals of the alkoxides of tin to a certain extent never appeared even when the mixture was allowed to cool for 24 hours, but instead, yellowish solutions in the alcohols were obtained. The crystals were later obtained after distillation of the solution. This behaviour may mean that the alkoxide of tin is essentially covalent. Thus tin may have the tendency of expanding its coordination number in which case conventional two-electron covalent bonding may take place or through dative bonding with oxygen of the alkyl groups.

Although the role of the catalyst, mercury (II) chloride is sometimes assumed to be merely for cleaning the metal surface, the reactions of cleaned magnesium ribbon and tin foil with the alcohols alone without the catalyst, should have produced some alkoxides but in these experiments no product was obtained. Therefore it can be deduced that the role of the catalyst, in addition to cleaning metal surface might involve formation of metal amalgams, an activated intermediate derivatives which then readily react with alcohols. The catalyst is readily soluble in the alcohols. As observed in experiment 3.2.5 and 3.2. 9 addition of more of the catalyst resulted in the production of more tin ethoxide and isopropoxide as indicated by the deepening colour changes.

4.11 Conclusions and recommendations

The direct reactions of elemental metals Na, Mg, Al and Sn with dry ethanol and isopropanol successfully yielded the expected alkoxides which have been found to be in good agreement with the reported literature values[2, 22, 25, 32]. These reactions were found to decrease with increase in the electronegativity of the metals. Of these metals sodium being the least electronegative metal reacted fastest with the alcohols than tin which is more electronegative and its reactions were slowest and had to take place in the presence of a catalyst and heat.

It was also found that reaction with dry ethanol was faster than that with dry isopropanol. This indicates therefore that the more branched the alcohol molecule the lesser is its acidity due to the +I inductive effect of the aklyl groups and thus the slower the reaction with the metals.

Tin ethoxide and isopropoxide were directly prepared by the reaction of tin with dry ethanol and isopropanol respectively using the same inorganic catalyst, mercury (II) chloride. These products were found to be highly soluble in the corresponding alcohols producing yellowish solution which on careful drying produced pure ethoxide and isopropoxide. Alkoxides of Na, Mg and Al are partially soluble in the two alcohols. It was also found that increasing the catalyst concentration increased the amount of product.

From all the above findings it can be recommended that although the direct synthesis of metal alkoxides offers a means of achievement of products with higher degree of purity, the method should be restricted to the least electronegative metals in order that time is saved and much yield of product is obtained such that not much of this catalyst is used as it may easily give way to formation of some unwanted stable intermediate products or complexes in addition to the favoured alkoxide.

References

1. Bradley, D.C.Chem.Rev.1989,89, 1317

2. Bradley, D.C., Mehrotra, R.C .and Gaur, P.D. Metal alkoxides, Academic Press Inc. Ltd., London , New York, San Francisco, 1978, PP. 10 - 41, 46 - 58 .116- 121

3. Hubert -Pfalzgraf, L.G.and Canlton, K. G. Chem. Rev. 1990, 90, 969 - 995

4. Bradley,D.C., Mehrotra, R.C., Swanwick, J.D. and Wardlaw W.J. Chem. Soc. 1953, 6, 2025.

5. Bradley, D.C., Mehrotra,R.C. and Wardlaw, W. J.Chem.Soc.1952,6,5020.

6. Bradley, D.C.,Mehrotra,R.C. and Wardlaw, W.J.Cehm. Soc. 1952, 6,4204.

7. Vandersluys,W.G. and Sattelberger,A.P. Chem. Rev.1990,90,1027-1040

8. Liptrot, G.F. Modern inorganic chemistry, 2nd edition, Mills & Boon Ltd, London, 1974, PP. 146, 174, 187, 193, 199 - 210, 213, 234 - 243.

9. Kreen,W.R., Rogers, M.J.W. and Simpson, P. Chemistry: Facts, patterns and principles, Revised edition, Addison-Wesly Publishers, London, 1984, PP. 337, 339, 348, 363, 375

10. Cotton, F. A. And Wilkinson, G. Advanced Inorganic Chemistry, 3rd edition, Interscience Publishers, New York , 1972, PP 115, 189, 215 - 217.

11. Lee, J.D. A new concise inorganic chemistry,3rd edition, Van Nostrand Reinhold Company Ltd, London, 1977, PP. 146 - 147

12. Masterton, W. L. Slowinski, E.J. and Stanitski, C. L. Chemical Principles, 5th edition, Saunders College Publishing,Philadelphia, 1981, PP. 223.

13. Heslop, R.B. and Jones, K. Inorganic chemistry: A Guide to advanced study, Elsevier Scientific Publishing Company ,Amsterdam-Oxford-New York,1976, PP.318.

14. Baumgorten, R. L. Organic chemistry: Abrief survey, John Wiley and Sons, New York, 1978, PP. 191 - 192.

15. Norman, R.O.C. Principles of Organic Synthesis, 2nd edition, Chapman and Hall, NewYork, 1980, PP. 204 - 205.

16. Chang, R. Chemistry 2nd edition, Random House,New York, 1984, PP. 639.

17. Bell, C.F and Lott,K.A.K. Modern approach to inorganic chemistry, 3rd edition, Butterworth & Co. Ltd, London, 1972, PP. 273 -274.

18. Sneed, M.C. and Brasted, R.C. Comprehensive inorganic chemistry,Vol VII, D. Van Nostrand Company Inc. New York, 1958, PP 213- 214.

19. Jones,G.E.M. and Hughes, O.L. J.Chem.Sec.,1197 (1934)

20. Finar.I.L.Organic chemistry, 5th edition, Longmans Green and Company Ltd, London, 1966, PP. 149.

21. Morrison, R.T. and Boyd, R.N. Organicchemistry, 3rd edition, Allyn and Bacon Inc. Boston, London, Sydney, Toronto, 1981 PP. 1039 1041.

22. Cerchez, V. Bull. Soc. Chim., 43, 762 (1928)

23. Cohen, C.A.US Patent, 2,287,088(1943):Chem.Abstr. 37, 141 (1943)

24. Sulayman, N.M. Msc. thesis, University of Khartoum,1995.

25. Vogel.A.I.Text-Book of practical organic chemistry ,4th edition, Longman Group Limited, London, 1980., PP. 269, 270., 280 - 281.

26. Gladstone, J.H. and Tribe, A.J.Chem. Soc. 39, 4(1881).

27. Verley, A. Bull. Soc. Chim., 37, 537(1925).

28. Shiner, V.J. and Whittaker, D. J. Amer. Chem. Soc., 1969, 90, 394.

29. Sulieman, A.A., Msc. thesis, University of Khartoum, 1987

30. Bradley, D.C., Mehrotra, R.C. and Wardlaw, W. J. Chem. Soc. 1952, 6, 2027

31. Hench, L.L. and West, J.K. Chem. Rev. 1990, 90 33 - 72

32. Shriner, R.L., Fuson,R.C. and Curtin, D.Y. The Systematic Identification of organic compounds, 5th edition, John Wiley & Sons ,Inc.New York,1964.

33. Barraclough, D.C.,Bradley, D.C.,Lewis, J. and Thomas, I. M. J.Chem. Soc., 2601(1961).

34. Szymanski, H.A. Interpreted infrared spectra, Vol. 2, Plenum Press Data Division, New York 1966.

35. Solomons T. W. G. Fundamentals of organic chemistry, 2nd edition, John Wiley & Sons. Inc. Canada, 1986, PP. 524 - 526.