The Laser Powered Pyrolysis
of
Metal Deposition Precursors

A thesis submitted by

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Statement

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry at the University of Leicester between October 1990 and September 1993. The work has not been submitted, for any other degree at this or any other university.

Signed. R. Finney Date: 23/8/93
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Last but by no means least, I would like to thank the Science and Engineering Research Council for my research studentship and also Dr. A. C. Jones for the endless supply of chemicals.
The work contained in this thesis may also be found in the following publications:

   Laser-powered Homogeneous Pyrolysis of Triisobutylgallane and Tri-tert-butylgallane.

   Exchange and Pyrolysis in Mixed Trialkylgallanes.

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Chapter One

Introduction
During the last decade there has been a significant renewal of interest concerning the pyrolysis mechanisms of the simple alkyl compounds of Group II and III metals [1]. This scientific activity is a direct consequence of these compounds being recognized as potential precursors for the manufacture of compound semiconductor materials and in other applications. For example, trimethylgallane, TMGa - a pyrophoric, moisture sensitive and highly toxic volatile liquid - is used in the production of gallium arsenide, GaAs.

Since the pioneering growth work of Manasevit in the 1960’s [2], compound semiconductors manufactured from Group II-VI and III-V elements have been widely studied, and they have found applications ranging from solar cells to lasers. The most important techniques available for the growth of these devices are: (i) liquid phase epitaxy (LPE), (ii) molecular beam epitaxy (MBE), and (iii) metal organic vapour phase epitaxy (MOVPE). An in-depth description of each of these methods is to be found in references 3 and 4. However, the attributes of each one will be briefly discussed in this chapter. Firstly, LPE is a technique used for the deposition of epitaxial layers from supersaturated solutions; only very simple apparatus is required to produce layers of high purity, but despite this, the thickness uniformity of the layers is often poor in quality. Another drawback associated with this technique is the difficulty involved in the growth of alloys containing both Al and In. In the MBE technique, elemental sources are evaporated at a controlled rate onto a heated substrate under ultra-high vacuum conditions. The advantages of this method are that alloys with abrupt interfaces can be produced and the growth process can be monitored as the crystal is built up one atomic layer at a time. Unfortunately, this technique is not commercially viable, in that it is expensive in terms of both the initial outlay and the operating costs. The growth of alloys containing As or P is also problematic because of the high volatility of these species.

By far the most important and versatile technique is MOVPE. It has great advantages over the other epitaxial methods in that virtually all Group II-VI and III-V
compound semiconductors, as well as ternary alloys such as GaInAs, of high purity and with abrupt interfaces can be produced. The MOVPE process is highly suitable for large scale industrial production, but several problems still remain in that the reagents needed are often expensive and hazardous, coupled with the fact that there are a large number of parameters which have to be precisely controlled to ensure the required standards. Table 1.1 lists a number of reactant combinations which can be used for the MOVPE growth of the listed compound semiconductors, together with some of their applications.

A typical MOVPE arrangement for the production of GaAs or any other compound semiconductor is illustrated in figure 1.1. The typical starting materials used to grow GaAs are trimethylgallane, \((\text{CH}_3)_3\text{Ga}\) (TMGa), for the Group III element and arsine, \(\text{AsH}_3\), for the Group V element. The TMGa is a liquid at room temperature and is contained in a stainless steel bubbler, where the carrier gas (\(\text{H}_2\)) is bubbled through. The TMGa vapour is then transported to the reaction chamber. Gaseous \(\text{AsH}_3\) is supplied either neat or diluted with hydrogen in a steel cylinder. The reactor pressures used are dependent upon the precise requirements; they may vary between atmospheric and a few torr (1 torr = 1 mm Hg = 133.3 N m\(^{-2}\)). The two gas streams are then mixed and directed by a system of baffles onto a heated graphite block, called a susceptor, which holds the substrate - a GaAs single crystal wafer. This reaction zone is inductively heated by rf coils, operating at approximately 450 KHz. When TMGa and \(\text{AsH}_3\) are heated up to temperatures in the range 873-973 K, they react to deposit high purity GaAs. This simple scheme is only the basis of the MOVPE process, in that temperature-controlled baths, flow controllers and valves that make up a real reactor have been excluded. The stoichiometry of this reaction was first reported by Manasevit [2] and is generally represented as:

\[(\text{CH}_3)_3\text{Ga} + \text{AsH}_3 \rightarrow \text{GaAs} + 3\text{CH}_4\]  \[1.1\]

Although a great deal of information about the MOVPE growth of compound semiconductors has been accumulated, as regards the purity of the reactants,
Table 1.1: Source Materials for the MOVPE Growth of Group III-V and Group II-VI Compound Semiconductors and their Uses (taken from reference [3]).

<table>
<thead>
<tr>
<th>REACTANTS</th>
<th>COMPOUND</th>
<th>APPLICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMGa + TMAI + AsH$_3$</td>
<td>AlGaAs</td>
<td>Lasers</td>
</tr>
<tr>
<td>TEGa + TMAA + AsH$_3$</td>
<td>GaAs</td>
<td>Waveguides</td>
</tr>
<tr>
<td>TMGa + AsH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEGa + AsH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMGa + TEIn + AsH$_3$</td>
<td>GaInAs</td>
<td>Lasers, Photodiodes</td>
</tr>
<tr>
<td>TMGa + TMIn + AsH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEGa + TEIn + AsH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMIn + PH$_3$</td>
<td>InP</td>
<td>MESFETs*</td>
</tr>
<tr>
<td>TEIn + PH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMZn + H$_2$S</td>
<td>ZnS</td>
<td>LEDs**</td>
</tr>
<tr>
<td>DEZn + H$_2$S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMZn + H$_2$Se</td>
<td>ZnSe</td>
<td>LEDs, Laser optics</td>
</tr>
<tr>
<td>DEZn + H$_2$Se</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMCd + DMTe</td>
<td>CdTe</td>
<td>Visible Light Detectors, Solar cells</td>
</tr>
</tbody>
</table>

* MESFET = metal semiconductor field effect transistor.
** LED = light emitting diode.
Figure 1.1: Schematic diagram of the essential elements of the MOVPE process.
the optimal temperature and pressure conditions, flow rates and the reactor design, this has generally been of a highly empirical nature. As a direct consequence of this, the problems of carbon contamination and premature parasitic gas phase reactions associated with the manufacture of certain compound semiconductors remain largely unsolved. The problems specific to each type of semiconductor material are described in subsequent chapters. Future advances in the semiconductor industry now rest heavily upon precursor molecule design rather than the experimental conditions employed. Recently there has been a shift in emphasis towards achieving a fundamental understanding of the precise mechanism of the growth process. A wide range of techniques that include: mass spectrometry of the reaction products, spectroscopic techniques to detect unstable intermediates, radical trapping, isotopic labelling and kinetic studies, have been applied in an attempt to clarify the contributions of various components e.g. homogeneous versus heterogeneous, intramolecular versus radical processes, initiation by metal alkyl or Group V precursor, etc.

The pyrolysis experiments presented in this thesis were carried out using the method of Infrared Laser Powered Homogeneous Pyrolysis (IR LPHP), which has been shown to be highly suitable for studying the thermal decomposition of organometallic compounds [5,6]. This technique is unique in that a highly inhomogeneous temperature distribution is generated within the reaction cell. This means that temperatures as high as 1500 K can be reached at the centre of the cell, while the cell walls remain at room temperature, thus allowing the unstable primary reaction products to rapidly migrate into the cooler regions of the cell on formation. Hence the IR LPHP technique has provided valuable information about the fate of the metal containing fragments in pyrolysis reactions, while workers using more conventional methods have had to draw somewhat speculative conclusions from the observed hydrocarbon products and the composition of deposited solids.

In Chapter Two the chemical reagents used are listed and the experimental
equipment, together with the specifications of the IR LPHP technique, are described in
detail. The results of the IR LPHP of some of the simple alkyl compounds of Ga, B,
In, and Zn are presented in Chapters 3-6. The gas phase exchange reactions between
mixtures of dimethylalane, DMAIH, and trimethylalane, TMAI, form the basis of
Chapter 7. This study is of great interest to the growth of semiconductors because
facile reactions of this type are widely thought to be a source of carbon contamination
in deposited films. Finally, Chapter 8 draws together all the conclusions reached from
the above studies.

**Note on nomenclature.**

The names most commonly used in the semiconductor industry for many of the
compounds used in the experiments presented in this thesis are not those preferred by
the International Union of Pure and Applied Chemistry; moreover, the materials are
widely referred to by acronyms. For example, triethylgallane, \((\text{CH}_3\text{CH}_2)_3\text{Ga}\), is
triethyl gallium, TEGa. A full list of all chemical reagents used, together with their
acronyms, is shown in table 2.1 in Chapter 2.
REFERENCES


Chapter Two
Experimental
2.1 Introduction

In this chapter the chemical reagents, the experimental techniques and the equipment used for all the experiments will be described. The majority of the equipment, in particular the experimental arrangement for the Infrared Laser Powered Homogeneous Pyrolysis or IR LPHP, was originally designed by Atiya [1], with more recent modifications by Grady [2].

2.2 Chemicals

In tables 2.1 and 2.2 the chemicals purchased for the experiments and those which were synthesized are listed. Their common acronyms are also given as the compounds will often be abbreviated to these in the text. Dimethylalane and its deuterated isotopomers and fully deuterated trimethylalane were synthesized at Leicester, the details of which can be found in Chapter 7. The chemicals from Epichem Ltd. were gifts. The IR assignments for the hydrocarbon products observed in the IR LPHP studies were taken from references 3 and 4.

2.3 The Vacuum Line

The organometallic compounds used in the experiments are all extremely pyrophoric, moisture sensitive, and highly toxic liquids; therefore vacuum line techniques were employed. The vacuum line used is illustrated in figure 2.1; it was designed by Grady [2]. The manifold was constructed from Pyrex glass, which was 2 mm thick and 15 mm in diameter. The line was fitted with J. Young ‘O’ ring vacuum taps and P.T.F.E high vacuum screw cap joints. Only greaseless vacuum taps were used, as the organometallics were found to react with silicone grease. The sample tubes and reaction cells were connected to the line via the P.T.F.E screw cap joints. From figure 2.1 it can be seen that this line was specially constructed so that sections can be isolated in order for cell filling and static distillations to be carried out.
Table 2.1: List of Organometallic Compounds Used.

<table>
<thead>
<tr>
<th>ACRONYM</th>
<th>NAME</th>
<th>FORMULA</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMAI</td>
<td>Trimethylalane</td>
<td>(CH₃)₃Al</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>dTMAI</td>
<td>Fully deuterated TMAI</td>
<td>(CD₃)₃Al</td>
<td>*</td>
</tr>
<tr>
<td>TMGa</td>
<td>Trimethylgallane</td>
<td>(CH₃)₃Ga</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>TMIn</td>
<td>Trimethyl indium</td>
<td>(CH₃)₃In</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>TEAl</td>
<td>Triethylalane</td>
<td>(C₂H₅)₃Al</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>TEB</td>
<td>Triethylborane</td>
<td>(C₂H₅)₃B</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>TEGa</td>
<td>Triethylgallane</td>
<td>(C₂H₅)₃Ga</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>TEIn</td>
<td>Triethyl indium</td>
<td>(C₂H₅)₃In</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>TIPGa</td>
<td>Triisopropylgallane</td>
<td>(C₃H₇)₃Ga</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>TIBGa</td>
<td>Triisobutylgallane</td>
<td>(C₄H₉)₃Ga</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>TTBGa</td>
<td>Tri-tert-butylgallane</td>
<td>(C₄H₉)₃Ga</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>DMAIH</td>
<td>Dimethylalane</td>
<td>(CH₃)₂AlH</td>
<td>*</td>
</tr>
<tr>
<td>DMAID</td>
<td>Dimethyldeuteroalane</td>
<td>(CH₃)₂AlD</td>
<td>*</td>
</tr>
<tr>
<td>d₆-DMAIH</td>
<td>Di(perdeuteromethyl)alane</td>
<td>(CD₃)₂AlH</td>
<td>*</td>
</tr>
<tr>
<td>DMZn</td>
<td>Dimethyl zinc</td>
<td>(CH₃)₂Zn</td>
<td>Epichem Ltd.</td>
</tr>
<tr>
<td>DEZn</td>
<td>Diethyl zinc</td>
<td>(C₂H₅)₂Zn</td>
<td>Epichem Ltd.</td>
</tr>
</tbody>
</table>

* Synthesis described in Chapter 7.
<table>
<thead>
<tr>
<th>NAME</th>
<th>FORMULA</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Hydride</td>
<td>CaH₂</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>C₅H₁₀</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>C₆H₁₄</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>2,3-Dimethylhexane</td>
<td>C₈H₁₈</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Ethene</td>
<td>C₂H₄</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>d₅-Pyridine</td>
<td>C₅D₅N</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>d₈-Toluene</td>
<td>C₇D₈</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Sulphur Hexafluoride</td>
<td>SF₆</td>
<td>B. O. C. Ltd.</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>(CH₃)₃N</td>
<td>Aldrich Chemical Co.</td>
</tr>
</tbody>
</table>
At the far end of the manifold was a U-trap cooled by liquid nitrogen; this prevented any of the compounds entering the oil of the pumps. The line was equipped with two pumps: an Edwards EO2 oil diffusion pump (Dow Corning 702 silicone oil) and an Edwards E2M5 two-stage rotary pump. The typical vacuum obtained using the rotary pump was around $10^{-2}$ mbar; however, with the oil diffusion pump $10^{-5}$ mbar could be attained. This vacuum was measured using two gauges: a Pirani PRL10K gauge (for pressures in the range $10^{-4}$ mbar) and a Penning CP25K gauge for measuring lower pressures more accurately. Measurement of the pressures of samples introduced into the line was carried out using a MKS-122A baratron (of range 0-100 torr).

2.4 Sample Preparation

The organometallic compounds after removal from their respective cylinders were distilled and stored under vacuum in standard Pyrex sample tubes, which were kept in a fire proof cabinet. The photosensitiser gas, SF$_6$, was stored in the U-tube on the vacuum line. It was filled directly from the cylinder via the port shown in figure 2.1. Prior to each experiment, the SF$_6$ was pumped on at 77 K, in order to remove any oxygen present; this was then followed by the removal of residual water vapour at 197 K. The NMR solvents: cyclopentane, d$_3$-pyridine, and d$_8$-toluene, were all dried and stored over calcium hydride.

Before commencing each experiment, all the samples were subjected to several freeze-pump-thaw cycles at 77 K; the purpose of this was to remove any traces of oxygen or decomposition products. This is particularly important for the organometallic compounds as leakage of air through the vacuum tap causes the production of hydrocarbons from subsequent hydrolysis and/or oxidation.

Before filling the reaction cell, residual adsorbed water or oxygen were removed by conditioning the reaction cell and the vacuum line with a small pressure of the organometallic compound to be studied. After several minutes both the reaction cell
and the vacuum line were evacuated and then the reaction cell was filled with the required pressure of the reactant gas or gases. An FTIR spectrum of the contents of the cell was then recorded.

All pyrolysis studies were carried out using the technique of Infrared Laser Powered Homogeneous Pyrolysis, to be described in the next section.

2.5 Infrared Laser Powered Homogeneous Pyrolysis

2.5.1 Introduction

Since the discovery of the first laser, based on the transitions in ruby (Al₂O₃ doped with Cr³⁺) in 1960, the huge potential of lasers, particularly in the promotion of chemical reactions, has been greatly developed. Early experiments, however, were inhibited by the requirement for there to be a direct match in energy levels between the laser output and the absorbing reactant molecule. This problem was successfully overcome by Tardieu de Maleissye in 1972, when he reported the first example of the use of an inert photosensitiser [5]. Tardieu de Maleissye and co-workers pyrolysed both ethyne and ethane (which are non-absorbing molecules) in the presence of the photosensitiser, SF⁶, using the infrared carbon dioxide laser [6]. The basic principle of this method is that a specific vibrational mode of the photosensitiser absorbs energy from the laser radiation and then rapidly converts this energy into heat (translational energy) via efficient relaxation processes. This heat energy is subsequently transferred to the reagent molecules via collisions; in this respect it is very similar to conventional pyrolysis techniques, and this process is therefore known as Infrared Laser Powered Homogeneous Pyrolysis or IR LPHP.

The major advantage of this technique is that it is an entirely homogeneous process, in that energy is transferred directly into the gas phase. This generates a static temperature profile in which the centre of the pyrolysis cell may reach as high as 1500 K, while the cell walls remain at room temperature. However, the disadvantage associated with the production of this non-uniform temperature distribution is that
detailed kinetic data cannot be derived. Despite this the IR LPHP process still has significant advantages over conventional ‘hot-walled’ pyrolysis techniques, where the principle drawbacks are that the primary reaction products tend to decompose on the reactor walls and that this deposition of solid material may provide a highly auto-catalytic surface for further reaction. This was clearly demonstrated by Ashworth et al. in the oxidation of tetramethyl tin [7]. The inability to trap primary products, such as free radicals, means that purely conjectural reaction mechanisms are deduced from the final products, which are usually hydrocarbons and deposited materials.

Following the pioneering work of Tardieu de Maleissye et al. this technique was further developed by a number of workers, chiefly: Shaub and Bauer [8], Smith et al. [9], Pola [10], and Zitter and Koster [11]. The IR LPHP technique has been extensively reviewed in a recent article by Russell [12], in which more detailed information is to be found. In this chapter only the essential elements of the IR LPHP technique which were used to carry out the pyrolysis experiments presented in this thesis are to be described.

2.5.2 Experimental Equipment

The typical apparatus used for an IR LPHP experiment is illustrated in figure 2.2. In each investigation a few torr of the target gas or gases, together with 10 torr of SF$_6$ (photosensitiser), is contained in a cylindrical Pyrex cell of volume ~100 cm$^3$. Apart from the filling port, there may be an additional port for the attachment of an NMR tube. For organometallic compounds of low volatility (vapour pressure < 0.5 torr), such as triisopropylgallane, the cylindrical hollow of the cell shown in figure 2.2 is cooled to 77 K, thus allowing the condensation of a small amount of liquid sample. This feature enables stronger FTIR spectra of the species involved to be detected; this is achieved by the gentle warming of this hollow using a hairdryer, with the result that the compound is distilled onto the cell windows. The cell is then exposed to the output of the carbon dioxide gas laser, while changes in the cell contents are
Figure 2.2: Schematic diagram of the essential elements of the IR LPHP process.
monitored using FTIR spectroscopy at selected time intervals. Each piece of equipment used in a typical IR LPHP experiment will now be described in detail below.

2.5.3 Reaction Cells

The two main designs of reaction cell which were used for the experiments are shown in figures 2.2 and 2.3. These cylindrical cells were made of 2 mm thick Pyrex and each was fitted with a J. Young 'O' ring vacuum tap. Zinc selenide windows were attached to both ends using quick-set Epoxy Resin.

Samples for \(^1\)H NMR spectroscopy were prepared either by attaching an NMR tube directly to the cell illustrated in figure 2.2 or alternatively by connecting both the reaction cell shown in figure 2.3 and the NMR tube to the specially designed H-shaped adapter illustrated in figure 2.4. J. Young NMR tubes were used; these were fitted with greaseless, rotationally symmetrical valves. The valves were vacuum sealed to the port by 'O' rings.

2.5.4 Window materials

The main reasons why ZnSe windows were used in all the IR LPHP experiments, was because they possess the following properties:

i) highly transparent for infrared radiation from both the CO\(_2\) laser and the FTIR spectrometer;

ii) good mechanical strength means long durability;

iii) high thermal stability;

iv) high thermal conductivity;

v) low thermal expansion;

vi) chemically inert;

vii) non-hygroscopic nature.

The disadvantages associated with the use of ZnSe windows include that they have
Figure 2.3: Schematic diagram of a standard reaction cell.
Figure 2.4: Schematic diagram of the H-shaped adapter.
a high cut-off (500 cm\(^{-1}\)) and they are expensive; this is not only because of the intrinsically cost of the ZnSe, but also because they possess a high refractive index and hence need to have an anti-reflection coating of Al\(_2\)O\(_3\). However, in comparison with the cheaper alkali halide materials, which often suffer severe thermal stresses during laser pyrolysis [13] and together with their hygroscopic nature which may cause the hydrolysis of moisture sensitive organometallics, ZnSe windows do offer a distinct advantage [14].

2.5.5 Photosensitisers

The most commonly used photosensitiser, SF\(_6\), was used for all the IR LPHP experiments in the present work. Other workers have used SiF\(_4\) [15], C\(_6\)F\(_6\) [16] and NH\(_3\) [17] successfully as photosensitisers. Of these only SiF\(_4\) has found widespread use; it is thermally more stable than SF\(_6\) (the SF\(_5\)-F bond dissociation enthalpy is 389 kJ mol\(^{-1}\), while for the SiF\(_3\)-F bond it is 594 kJ mol\(^{-1}\)), but despite this fact it is a somewhat poorer absorber of infrared radiation and is also moisture sensitive.

SF\(_6\) is ideal as a photosensitiser because it has the following characteristics:

i) very strong absorption of the infrared CO\(_2\) laser radiation;

ii) very rapid intramolecular vibration-vibration and vibration-rotation/translational energy conversion, and very efficient intermolecular energy transfer;

iii) high thermal stability (well above temperatures of 1200 K [18]);

iv) chemically inert (difficult for nucleophiles such as water to attack a symmetrical octahedron [19]);

v) low thermal conductivity; this permits the generation of highly inhomogeneous temperature profiles at modest laser powers.

In the present work the SF\(_6\) did not participate in any of the chemical reactions. However, there are two examples where SF\(_6\) has played a significant chemical role: firstly, in the pyrolysis of CH\(_3\)SiCl\(_3\) by Pola et al. [20], and secondly in the IR LPHP of TMAI by Atiya [1]. These observations can be explained in terms of the
exceptional strengths of the Si-F and Al-F bonds respectively [21].

The precise mechanism of how the SF$_6$ absorbs and transfers the CO$_2$ laser radiation will be discussed in section 2.8 below.

2.6 The Carbon Dioxide Laser

An Edinburgh Instruments PL4 free-running carbon dioxide gas laser was used for the IR LPHP experiments [22]. A schematic diagram of the CO$_2$ laser is illustrated in figure 2.5. The main components of this are: a Pyrex discharge tube, 130 cm in length (D), which is sealed at both ends with anti-reflection coated ZnSe windows (W); these allow the transmission of 10.6 $\mu$m of IR radiation. There is a cavity 180 cm in length; this has a rear mirror (M) and an output coupling mirror (OC), which possesses reflectivity of 75%. This output coupling mirror (OC) is mounted on a piezo-electric transducer (PZT), which by its adjustment the cavity can be fine tuned and stabilized.

The laser was operated using a mixture of: 9% CO$_2$, 13.5% N$_2$ and 77.5% He, which is pumped through the discharge tube continuously. The pressure inside the discharge tube was controlled by a meter valve (MV) and measured by a vacuum gauge (G), connected to the outlet of the discharge tube, which in turn was fitted to a rotary pump (Edwards ESM2). A continuous flow of gas mixture is used because it not only cools the laser, but serves to remove vibrationally excited gas, impurities and discharge products, all of which may affect laser output. Further cooling of the discharge tube is provided by the water jacket (C).

An Edinburgh (PS4R) power supply provided the electric discharge, rated at 30 kV and 30 mA. Laser powers of between 0.5-50 watts (IR radiation of 10.6 $\mu$m) were obtained by varying both the pressure of the laser gas and the current supplied. The emergent beam had a diameter of 7.5 mm with a divergence of less than 2 milliradians. A Coherent Power meter, Model 201, was used to monitor the laser power. This was calibrated to give a signal of 0.4 mV/watt of power absorbed and its rise time was approximately 1 second.
Figure 2.5: Schematic diagram of the CO$_2$ laser.
2.6.1 Basic principles of operation of the CO₂ gas laser

The carbon dioxide laser is a mid infrared gas laser, which is capable of immense power and has an efficiency of approximately 20%. It operates on the vibrational energy levels in the carbon dioxide molecule, as opposed to other types of laser, such as the helium-neon laser, which is based on transitions between electronic levels [23].

On passing an electric discharge through the carbon dioxide laser gas mixture, helium produces electrons and it is these which cause the nitrogen molecules to become vibrationally excited to the v=1 level by electronic and ionic collisions. This is metastable as transitions back down to the v=0 level are forbidden. The v=1 vibrational level of nitrogen almost coincides with the antisymmetric stretching (001) vibrational energy level of CO₂, which picks up the energy during a collision. This results in a population inversion and subsequent collisions with the helium atoms in the gas mixture causes laser action to take place between the (001) level of CO₂ and the unpopulated lowest excited level of the symmetric stretch (100) and the second lowest excited level of the CO₂ bending mode (020). This generates 10.6 μm and 9.6 μm of infrared radiation respectively. A block diagram of the vibrational energy levels used in the CO₂ laser is shown in figure 2.6.

2.7 Monitoring of the Reaction

The progress of the pyrolysis reaction can be monitored using any analytical technique, including mass spectrometry or gas chromatography. However, the vast majority of workers have opted for the non-invasive technique of Fourier Transform Infrared Spectroscopy (FTIR). In the next section the basic principles of how the FTIR spectrometer operates will be discussed, together with the advantages of using high field Fourier Transform NMR Spectroscopy for product analysis.
Figure 2.6: Block diagram of the vibrational energy levels of importance in the CO$_2$ laser.
2.7.1 Fourier Transform Infrared Spectroscopy

All the infrared spectra presented in this thesis were recorded using a Digilab FTS40 FTIR spectrometer at a resolution of 2 cm\(^{-1}\).

The FTIR spectrometer works on the basic principle that infrared light from a suitable source passes through a scanning Michelson interferometer and Fourier Transformation provides a plot of intensity versus frequency [24]. When a sample is placed in the beam it absorbs particular frequencies, so that their intensities are reduced in the interferogram and the subsequent Fourier Transform is the infrared absorption spectrum of the sample.

The speed with which the infrared spectrum can be attained is dictated by the scan time of the moving mirror (the key part of the interferometer), plus the digitisation of the data and the calculation of the Fourier Transform, but despite all this the spectrum can be acquired within seconds. The FTIR spectrometer allows the accumulation of up to 1000 scans, thus improving significantly signal to noise ratios.

The advantages of FTIR over conventional IR spectrometers can be summarized as follows:

i) increased sensitivity compared to conventional spectrometers where most of the light from the source gets lost in the narrowness of the focusing slits;

ii) greater speed of data acquisition - able to scan whole wavelength range in one short scan;

iii) excellent levels of accuracy - conventional machines suffer from wavelength inaccuracies due to backlash from mechanical movements, such as rotation of mirrors or gratings, whereas FTIR spectrometers use continuous calibration by internal He/Ne laser;

iv) fewer moving parts, therefore less susceptible to vibrations;

v) computer manipulation of spectra, for example, water vapour can be subtracted out of spectrum.
2.7.2 Fourier Transform NMR Spectroscopy

All the ¹H NMR spectra presented in this thesis were recorded at 300 MHz using a Bruker AM300 FT-NMR spectrometer.

Fourier Transform NMR Spectroscopy offers similar advantages as Fourier Transform IR Spectroscopy, in terms of both the speed of acquisition of spectra and the computer manipulation of spectra [25]. In the present work high field ¹H NMR spectroscopy has been extremely instrumental in confirming all the conclusions drawn from the infrared spectroscopic observations. The main areas of importance have included:

i) high sensitivity for samples at low concentrations (mg quantities);

ii) double resonance techniques, e.g. spin decoupling; this was particularly helpful in the TEGa + TMGa system, described in Chapter 3;

iii) detection of alkyl groups on different metal centres; this was essential in the exchange reactions studied, see Chapters 3 and 7;

iv) accurate measurement of integrals; this enabled the relative abundances of hydrocarbon pyrolysis products to be calculated. This was of great interest in the TEIn system (Chapter 5);

v) the most important feature of the Bruker AM300 FT-NMR spectrometer was the variable temperature probe; this uses cold N₂ gas from boiling liquid N₂ and an electric heater, to produce temperatures as low as 191 K. Temperatures were produced with an estimated accuracy of 1-2 K. The most significant uses of this were that at low temperatures spectra of thermolabile materials, such as dialkylgallanes, could be recorded and exchange reactions as in the TEGa + TMGa and TMAI + DMAIH mixtures could be investigated over a whole range of temperatures.

2.8 Absorption and Disposal of Laser Energy

A number of detailed experimental and theoretical investigations have been carried out as regards the precise mechanics of the IR LPHP technique. These studies have
centred around three main areas: the mechanism of infrared radiation absorption by
the photosensitiser, the transfer of this energy with the subsequent production of heat
energy, and the shape of the temperature profile generated. Details of these studies
may be found in the IR LPHP review by Russell [12].

Table 2.3 lists the infrared active bands of the SF\textsubscript{6} molecule, together with their
assignments. Figure 2.7 shows an FTIR spectrum recorded of 10 torr of SF\textsubscript{6}. Nowak
and Lyman in 1975 investigated the interaction of the photosensitiser, SF\textsubscript{6}, with CO\textsubscript{2}
laser radiation [27]. These workers found that the SF\textsubscript{6} molecule has an extremely high
absorption for a significant number of lines in the CO\textsubscript{2} laser spectrum. At room
temperature a maximum absorption of $1.8 \times 10^{7} \text{ mol}^{-1} \text{ cm}^{2}$ was recorded for the
10P(16) line near 948 cm\textsuperscript{-1}. Therefore IR laser radiation is absorbed by SF\textsubscript{6} into the
$\nu_{3}$ triply degenerate S-F stretching vibration. If the effects of both bleaching and
temperature are disregarded, this results in an absorption of $>99.5\%$ of the incident
laser light over a path length of 5 mm, using 10 torr of SF\textsubscript{6}.

The most important information as far as IR LPHP is concerned is not the fate of
the absorbed infrared energy, but the rate at which it appears as heat (translational
energy) in the system. Recently Sugawara and co-workers reported the vibrational
relaxation time of SF\textsubscript{6} to be $10 \mu s$ torr [28]. This was measured by using a pulsed TEA
CO\textsubscript{2} laser and infrared diode laser spectroscopy on mixtures of CO and SF\textsubscript{6}. From
this work it can be concluded that infrared radiation absorbed by 10 torr of SF\textsubscript{6}, will
appear as heat in the reaction cell within $1 \mu s$.

2.9 Temperature Distribution

As previously mentioned, the generation of a highly inhomogeneous temperature
profile within the reaction cell is one of the most significant features of the IR LPHP
technique. It is this feature that permits the detection and isolation of primary reaction
products; for example in the IR LPHP of TEGa, the unstable diethylgallane formed
condenses onto the cool walls of the reaction cell, where it is not subject to further
<table>
<thead>
<tr>
<th>Wavenumbers</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1718 (m)</td>
<td>$\nu_1 + \nu_3$</td>
</tr>
<tr>
<td>1587 (m)</td>
<td>$\nu_1 + \nu_2$</td>
</tr>
<tr>
<td>1387 (w)</td>
<td>$\nu_1 + \nu_4$</td>
</tr>
<tr>
<td>1282 (w)</td>
<td>$2\nu_2$</td>
</tr>
<tr>
<td>1255 (mw)</td>
<td>$\nu_2 + \nu_4$</td>
</tr>
<tr>
<td>1137 (vw)</td>
<td>$\nu_4 + \nu_5$</td>
</tr>
<tr>
<td>985 (s)</td>
<td>$\nu_2 + \nu_6$</td>
</tr>
<tr>
<td>948 (vvs)**</td>
<td>$\nu_3$</td>
</tr>
<tr>
<td>885 (m)</td>
<td>$\nu_5 + \nu_6$</td>
</tr>
<tr>
<td>869 (m)</td>
<td>$\nu_5 + \nu_6$</td>
</tr>
<tr>
<td>856 (m)</td>
<td>$\nu_5 + \nu_6$</td>
</tr>
<tr>
<td>625 (vs)</td>
<td>$\nu_4$</td>
</tr>
<tr>
<td>615 (vs)</td>
<td>$\nu_4$</td>
</tr>
<tr>
<td>604 (vs)</td>
<td>$\nu_4$</td>
</tr>
</tbody>
</table>

* s=strong, m=medium, w=weak, v=very, br=broad, sh=shoulder; v=stretch, δ=deformation, ρ=rock, sym=symmetric, as=asymmetric.

# Assignments are those of reference [26] and in this case ν represents symmetry labels only.

** Transition resonant with CO$_2$ laser output.
Figure 2.7: FTIR spectrum of 10 torr of SF$_6$. Arrows = CO$_2$ laser output.
reaction [2]. However, the non-uniform temperature distribution is also the main drawback associated with this technique, since rates of reactions are dependent on temperature; the amount of kinetic data which can be gleaned is therefore limited. For this reason, there have been numerous investigations of this profile, using a variety of methods including: chemical thermometers [8], interferometry [29], thermocouples [30,31], and tunable IR diode laser spectroscopy [1].

Calculating the temperature distribution is a complex problem because of the number of variables that have to be taken into account. These include the extent of laser radiation absorption by SF$_6$, which is dependent upon the power, temperature and the density, together with the effects of conduction, convection and heat released during chemical reactions. Therefore an accurate measurement of the temperature profile is severely hampered by its extreme sensitivity to the experimental conditions employed. However, the recent use of pulsed excitation has helped to overcome some of the difficulties experienced. The experimental details of this technique are to be found in several articles by McMillen et al. [32].

In our own laboratory, Atiya investigated the temperature distribution which is produced using a CO$_2$ laser and SF$_6$ as photosensitiser [1]. Three different methods were used:

i) a visual determination of the reaction area was made by photographing the emission of iodine atoms produced in a chemiluminescent reaction.

ii) tunable IR diode laser spectroscopy was used to record the vibration-rotation components of a CO (<0.5 torr) and SF$_6$ mixture, during CO$_2$ laser irradiation. Figure 2.8 illustrates the isotherm obtained and figure 2.9 shows the plot of mean temperature along the probe beam path through the axis of the cell versus laser power for two positions along the cell, which was measured.

iii) ethyl ethanoate was used as a chemical thermometer, since its kinetic parameters are well known. The results obtained when 10 torr of ethyl ethanoate and 10 torr of SF$_6$ were pyrolysed are also presented in figure 2.9. This mixture was irradiated at a
Figure 2.8: Schematic isotherm of the laser-heated gas mixture.
Figure 2.9: Temperature as a function of laser power in IR LPHP measured by tunable IR diode laser spectroscopy at the cell entrance window (●) and 3.8 cm from the window (★). For comparison, temperatures estimated using CH$_3$COOC$_2$H$_5$ as a chemical thermometer are also presented (★). Taken from reference [1].
number of different laser powers and the reaction was monitored by FTIR spectroscopy. The initial rate of this first order reaction was recorded at all powers.

Atiya was able to draw the following conclusions based on the results of all three experimental methods: the temperature produced by the CO$_2$ laser radiation is clearly non-uniform throughout the reaction cell, while the hottest part of the cell is to be found some 1 cm from the entrance window, and that the temperature distribution is cylindrically symmetrical.

Despite the fact that the use of the chemical standard, ethyl ethanoate, can only at best yield spatially averaged temperatures, these results do serve as a valuable estimate of the maximum cell temperatures achieved in the IR LPHP experiments presented in this thesis.

2.10 Summary of the IR LPHP Technique

The major advantages and disadvantages of the IR LPHP technique in comparison with conventional pyrolysis methods can be summarized as follows:

**Advantages**

i) Require only a few µg of sample, therefore both rare and expensive compounds can be studied.

ii) Only very simple experimental equipment is needed.

iii) Temperature of the system can be easily controlled and extremely high temperatures can be achieved within µseconds.

iv) Surface effects (loss or initiation) are thought to be negligible as the reaction takes place in the centre of the cell (the hot zone).

v) Purely homogeneous reactions, in that only gas phase processes play a part in the reaction initiation stage (except for liquid samples where the rate limiting step is the evaporation of the starting material).

vi) The non-uniform temperature profile generated means that the primary reaction products are rapidly ejected into the cool regions of the cell, thus enhancing their
lifetime and chances of detection.

Disadvantages

i) The generation of products alters both the heat capacity and the thermal conductivity of the system during a reaction, and therefore leads to a change in the temperature distribution.

ii) It is difficult to obtain detailed kinetic parameters due to the non-uniform temperature profile in the reaction cell.
REFERENCES


Chapter Three

IR LPHP of Triethylgallane and Trimethylgallane Mixtures
3.1 Introduction

The trialkyls of Group III have been extensively used for the growth of III-V semiconductor devices by metal organic vapour phase epitaxy (MOVPE) [1] and molecular beam epitaxy (MBE) [2]. There are however, several disadvantages associated with these simple precursors, principally being that trimethyl compounds, such as TMAI [3], lead to unwanted carbon incorporation in the deposited film, and triethyl compounds often have low volatility, which requires the heating of the reactor gas-inlet lines, causing premature decomposition and poor growth rates. A possible solution to these problems was thought to be the use of mixed alkyl group precursors, for example Me₂EtIn, which would combine the high volatility of the methyl compounds, with the reduced carbon incorporation of the ethyl compounds.

The main objectives set out in this chapter were firstly to examine alkyl group exchange reactions for trialkyl gallium compounds, with the aid of FTIR and ¹H NMR spectroscopies, and, more importantly, the IR LPHP of triethylgallane, TEGa and trimethylgallane, TMGa, mixtures was investigated. The aim of this was to selectively β-eliminate the ethyl groups, thus providing a synthetic route to dialkylgallanes and the novel monomethylgallane.

This chapter begins by reviewing previous studies which have been carried out on mixed alkyl group compounds; this is then followed by a synopsis of recent work from this group on the IR LPHP of both TEGa and TMGa. The work contained in this chapter is described in J. Mater. Chem., 1993, 3, 483.

3.2 Review

3.2.1 Introduction

At the present time there is limited information available concerning alkyl group exchange reactions in the gas phase, as previous studies have concentrated on ligand exchange in solution between mainly aluminium alkyls (reviewed in Chapter 7). In this review the most significant studies to date concerning mixed alkyl group compounds
of Al, Ga and In, have been divided into three sections.

3.2.2 Growth Studies Using Mixed Alkyl Group Precursors

Knauf and co-workers have successfully grown high purity InP and GaInAs layers, using the alternative indium precursor, EtMe$_2$In [5]. In this study a direct comparison of growth behaviour between EtMe$_2$In and Me$_3$In was made using a standard low pressure MOVPE reactor. It was found that at identical Me$_3$In and EtMe$_2$In partial pressures, the growth rate of InP was nearly 100% higher using the latter compound, which suggested that the higher growth efficiency was increased because of the lower thermal stability of the EtMe$_2$In.

The indium precursor, EtMe$_2$In, which is a liquid at room temperature, was first used to grow InP and GaInAs films in an atmospheric pressure MOVPE reactor. In this work, carried out by Fry et al. [6], the formation of extremely poor quality layers was reported.

An alternative aluminium precursor, $^t$BuMe$_2$Al, was used by Jones et al. to grow AlGaAs, in an atmospheric pressure MOVPE reactor [7]. It was thought that the presence of the bulky tertiary butyl group would inhibit the formation of oligomers, through which alkyl exchange occurs. However, the results obtained were somewhat disappointing, in that the $^t$BuMe$_2$Al may decompose in the reactor prior to growth, yielding dimethylalane, DMAIH and that despite layers of good optical quality being grown, the level of carbon contamination was approximately equal to that using TMAI. On the positive side, however, it was concluded that $^t$BuMe$_2$Al did show potential at low substrate temperatures.

3.2.3 Synthesis And Properties Of Mixed Alkyl Group Compounds

Bradley and co-workers have recently reported the synthesis of the following compounds: Me$_2$EtM, (Me$_2$EtM)$_2$ diphos and Me$_2$EtM.NMe$_3$, where M=Al, In; diphos=(Ph$_2$PCH$_2$)$_2$ [8]. These heteroleptic alkyls were prepared by reacting
Me₂MCl with EtMgBr in diethyl ether, followed by the formation of adducts with diphos. The white crystalline solids produced were heated to 353 K, whereupon colourless distillates of Me₂EtAl and Me₂EtIn formed. Variable temperature ¹H NMR spectra for both compounds revealed that rapid alkyl group exchange occurs and for Me₂EtIn this ligand exchange was so facile that it could not be frozen out at 193 K. Re-distillation of this compound, resulted initially in the formation of crystalline Me₃In, which is in agreement with the proposed disproportionation reaction in solution:

\[
3\text{Me}_2\text{EtIn} \rightarrow 3/2\text{Me}_3\text{In} + 3/2\text{MeEt}_2\text{In} \rightarrow 2\text{Me}_3\text{In} + \text{Et}_3\text{In} \quad [3.1]
\]

It was the opinion of these workers that the compounds formulated as Me₂EtAl and Me₂EtIn are not suitable precursors for MOVPE/MBE of III-V materials as the alkyl groups are too labile.

Barron and Cleaver [9] have prepared hybrid organometallic compounds of gallium by the reaction of the alkylating agent methyl lithium with a halogenated organogallium compound in hexane as shown below:

\[
\begin{align*}
2^t\text{Bu}_3\text{Ga} + \text{GaCl}_3 & \rightarrow 3^t\text{Bu}_2\text{GaCl} & [3.2] \\
^t\text{Bu}_3\text{Ga} + 2\text{GaCl}_3 & \rightarrow 3^t\text{BuGaCl}_2 & [3.3] \\
^t\text{Bu}_2\text{GaCl} + \text{MeLi} & \rightarrow ^t\text{Bu}_2\text{MeGa} + \text{LiCl} & [3.4] \\
^t\text{BuGaCl}_2 + 2\text{MeLi} & \rightarrow ^t\text{BuMe}_2\text{Ga} + 2\text{LiCl} & [3.5]
\end{align*}
\]

^tBu₂MeGa and ^tBuMe₂Ga are colourless pyrophoric liquids, which show little tendency to disproportionate in solution. A mass spectrometry study of these compounds revealed strong evidence to suggest they exist as monomeric three-coordinated gallium compounds. These workers are currently investigating the potential of these hybrid organogallium compounds for the MOVPE of GaAs films [10].

3.2.4 Decomposition Studies Of Mixed Trialkyl Compounds

The synthesis of the hybrid organogallium compounds ^tBu₂MeGa and ^tBuMe₂Ga
by Barron et al. has been described above. These workers have also investigated the
gas phase UV excimer laser induced photolysis of the aforementioned compounds
[11]. The photofragments Ga, GaH, and GaCH$_3$ were detected by laser ionisation
time-of-flight mass spectroscopy, while the hydrocarbon products were identified using
FTIR spectroscopy. The products of the photolysis of $^t$Bu$_2$MeGa were isobutene,
isobutane and methane in the ratio 1:0.45:0.2, while the products for $^t$BuMe$_2$Ga were
ethane, methane, isobutene and isobutane in the ratios 1:0.25:0.19:0.12 respectively.
Based on the results obtained Barron et al. have proposed that $\beta$-hydride elimination
only occurs after the photochemical fission of one of the more weakly bound Ga-$^t$Bu
bonds. This theory is in direct contrast to the results reported for the IR LPHP of
trialkyl gallanes [12,13]. The proposed mechanism is as follows:

For $^t$Bu$_2$MeGa

$$^t$$Bu$_2$MeGa $\rightarrow$ $^t$BuMeGa· + $^t$Bu· [3.6]

$$^t$$BuMeGa· $\rightarrow$ Me(H)Ga· + H$_2$C=C(CH$_3$)$_2$ [3.7]

For $^t$BuMe$_2$Ga

$$^t$$BuMe$_2$Ga $\rightarrow$ Me$_2$Ga· + $^t$Bu· [3.8]

Me$_2$Ga· $\rightarrow$ MeGa· + Me· etc. [3.9]

2Me· $\rightarrow$ C$_2$H$_6$ [3.10]

Me· + $^t$Bu· $\rightarrow$ CH$_4$ + H$_2$C=C(CH$_3$)$_2$ [3.11]

$^t$Bu· + $^t$Bu· $\rightarrow$ H$_2$C=C(CH$_3$)$_2$ + HC(CH$_3$)$_3$ [3.12]

Agnello and Ghandhi have studied the room temperature gas phase exchange
reaction between TMGa and TEIn [14]. The experiments were carried out in a
conventional low pressure MOVPE reactor and the reaction was monitored using mass
spectrometry. From their results Agnello et al. concluded that TMGa and TEIn not
only form an addition compound, but some alkyl group exchange occurs also. The
evidence for exchange comes from the observation of Me-In and Et-Ga peaks due to
Me$_2$In$^+$ and Et$_2$Ga$^+$, coupled with a reduction in the Me-Ga and Et-In peaks.
Signals attributed to EtMe$_2$Ga$^+$, MeEt$_2$Ga$^+$, and EtMe$_2$In$^+$ species were also
recorded. A dynamic structure was proposed for the TMGa-TEIn addition compound based on the data recorded: \( \text{Et}_2\text{In}(\mu\text{Me})(\mu\text{Et})\text{GaMe}_2 \). Repeated formation and dissociation of this structure could eventually lead to the formation of TMIn and TEGa.

A similar system was used to study a mixture of TEGa and TMAI using \( \text{H}_2 \) as carrier gas by Mashita et al. [15]. New species were produced in this system as a consequence of alkyl group exchange; these were clearly identified as \( \text{Me}_2\text{EtGa} \) and \( \text{MeEt}_2\text{Ga} \). These workers postulated that carbon incorporation would increase as a result of using mixed alkyl precursors, as the ethyl groups are easily lost at high temperatures leaving \( \text{MeGa}^- \) on the surface.

From the recent reports by Bradley and Barron described above, it can be concluded that mixed alkyl indium compounds are too labile, due to the weak In-C bond, and are thus unsuitable for growth work. On the other hand, compounds containing a bulky ligand such as a tertiary butyl group, where exchange is sterically unfavourable appear to offer potential as future gallium precursors.

### 3.2.5 Pyrolysis Studies of TMGa and TEGa

Previous studies of the mechanism of decomposition of TEGa, have been reviewed by Grady [12]. Detailed analysis has been carried out on the hydrocarbons produced (largely ethene, ethane and butane) by pyrolysis between 450-750 K. Two competing decomposition paths for TEGa have been proposed. These are:

1) The \( \beta \)-hydride elimination reaction where the Ga-C bond is replaced by a Ga-H bond with the formation of ethene;

\[
\begin{align*}
\text{Et}_3\text{Ga} & \rightarrow \text{Et}_2\text{GaH} + \text{C}_2\text{H}_4 & [3.13] \\
\text{Et}_2\text{GaH} & \rightarrow \text{EtGaH}_2 + \text{C}_2\text{H}_4 & [3.14] \\
\text{EtGaH}_2 & \rightarrow \text{Ga} + 3/2\text{H}_2 + \text{C}_2\text{H}_4 & [3.15]
\end{align*}
\]

Figure 3.1 shows the conformational structures illustrating the \( \beta \)-elimination reaction.
Figure 3.1: Structures illustrating the β-elimination reaction for TEGa.
2) A radical reaction involving the loss of ethyl radicals,

\[ \text{Et}_3\text{Ga} \rightarrow \text{Et}_2\text{Ga} \cdot + \text{Et} \cdot \quad \text{etc.} \quad [3.16] \]

and the production of ethane and butane,

\[ \text{Et} \cdot + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H} \cdot \quad \text{or} \quad [3.17] \]
\[ \text{Et} \cdot + \text{Et}_3\text{Ga} \rightarrow \text{C}_2\text{H}_6 + \text{Et}_2\text{GaC}_2\text{H}_4 \cdot \quad \text{and} \quad [3.18] \]
\[ \text{Et} \cdot + \text{Et} \cdot \rightarrow \text{C}_4\text{H}_{10} \quad [3.19] \]

The radical reaction is expected to only be significant at temperatures close to that used for TMGa, i.e. \( >600 \) K.

The IR LPHP of TEGa has been extensively studied by Grady [12]. This has resulted in the characterization of the major pyrolysis product, diethylgallane, by FTIR and \(^1\text{H}\) NMR spectroscopy. Figure 3.2 shows the FTIR spectrum of a mixture of TEGa (4 torr) and SF\(_6\) (10 torr), before (A) and after (B) exposure to 2 watts of CO\(_2\) laser radiation for a period of 60 seconds. FTIR and \(^1\text{H}\) NMR spectra of the NMe\(_3\) adducts of both diethylgallane and monoethylgallane were also recorded.

Table 3.1 summarizes the results obtained by various workers on the thermal decomposition of TMGa. Here, of course, the \( \beta \)-elimination route is not available, and the major reaction pathway undoubtedly involves methyl radicals. Jacko et al. [16] have proposed the following mechanism:

\[ \text{Me}_3\text{Ga} \rightarrow \text{Me}_2\text{Ga} \cdot + \text{Me} \cdot \quad [3.20] \]
\[ \text{Me}_2\text{Ga} \cdot \rightarrow \text{MeGa} \cdot + \text{Me} \cdot \quad [3.21] \]
\[ n(\text{MeGa} \cdot) \rightarrow (\text{MeGa} \cdot)_n \quad [3.22] \]
\[ 2\text{CH}_3 \cdot \rightarrow \text{C}_2\text{H}_6 \quad [3.23] \]

and the production of small amounts of ethene by:

\[ \text{CH}_3 \cdot + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 \cdot + \text{CH}_4 \quad [3.24] \]
\[ \text{C}_2\text{H}_5 \cdot \rightarrow \text{C}_2\text{H}_4 + \text{H} \cdot \quad [3.25] \]

In this postulated reaction scheme the rate limiting step is the slow removal of the first methyl group, followed by the much faster loss of the second, suggesting that the predominant gas phase metal-containing species would be GaMe. The IR LPHP of
Figure 3.2: FTIR spectra of a mixture of SF$_6$ (10 torr) and TEGa (3 torr), before (A) and after (B) irradiation at 2 W of laser power for 60 s. Features marked are assigned as follows: (O) = SF$_6$, (●) = Et$_2$GaH, and (●) = C$_2$H$_4$. 
<table>
<thead>
<tr>
<th>METHOD</th>
<th>TEMP(K)</th>
<th>PRODUCTS</th>
<th>ADDITIONAL COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot walled</td>
<td>643-843</td>
<td>Methane major product with traces of ethane, propane and butane. Reaction dependent on carrier gas used.</td>
<td>With H₂ carrier gas, mechanism proposed to be hydrogenolysis forming CH₄. Using N₂, homolytic fission of Ga-C bond and methyl radicals recombine [17].</td>
</tr>
<tr>
<td>Pyrex reactor using H₂ and N₂ as carrier gases.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Products examined by mass spec.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene carrier system, products analysed by G.C.</td>
<td>686-983</td>
<td>Methane major product, with smaller quantities of ethane and ethene.</td>
<td>Radical mechanism proposed: Me₃Ga → Me₂Ga⁺ + CH₃⁻ [16].</td>
</tr>
<tr>
<td>Exhaust from a MOVPE reactor monitored by IR, G.C. and mass spec.</td>
<td>1073</td>
<td>Methane only product.</td>
<td>Proposed that in this system the methyl radicals recombine with the gallium species to reform TMGa [18].</td>
</tr>
<tr>
<td>Sampled gases through pin hole in susceptor in a low pressure MOVPE reactor using mass spec.</td>
<td>550-850</td>
<td>Methane and ethane. Amount of ethane decreases above 725 K because of reaction with the carrier gas: CH₃⁻ + H₂ → CH₄ + H⁻ becomes major reaction path.</td>
<td>When D₂ was carrier gas CH₃D was the major product. A unimolecular radical mechanism was proposed, with the first step being the homolytic fission of Ga-C bond [19].</td>
</tr>
<tr>
<td>Differential Thermal Analysis. Products analysed by G.C.</td>
<td>623-773</td>
<td>At 623 K, 93% CH₄, 4% C₂H₄, 3% C₂H₆ and a trace of n-C₃H₁₀. At 773 K, 88% CH₄, 9% C₂H₄, 2% C₂H₆, 1% n-C₃H₁₀ and a trace of C₃H₈.</td>
<td>Few experimental details given. Free radical mechanism proposed as above [20].</td>
</tr>
</tbody>
</table>
TMGa has also been carried out by Grady et al. [21]. The major pyrolysis product from the FTIR study was methane. Figure 3.3 shows the FTIR spectrum of a mixture of TMGa (2 torr) and SF₆ (10 torr), before (A) and after (B) exposure to 4 watts of CO₂ laser radiation for 120 seconds. No gallium species corresponding to the trapping of either Me₂Ga or MeGa were observed, cf. Me₂AlF from the IR LPHP of TMAl by Atiya [22]; this is consistent with the lower Ga-F bond strength.

3.3 Experimental

Chemicals

The purification and handling of the TEGa and TMGa samples have been described in Chapter 2. The purity of TEGa, TMGa and NMe₃ were checked by FTIR and ¹H NMR spectroscopy. Tables 3.2, 3.3, and 3.4 report the IR spectra of the aforementioned reactants respectively. The ¹H NMR of NMe₃ gave a singlet at δₕ 2.06 ppm at 298 K.

Apparatus

All the experimental equipment used was described in Chapter 2.

3.4 Exchange Studies

3.4.1 Introduction

As a preliminary to the study of the pyrolysis of the TEGa + TMGa mixtures, the role of alkyl group exchange reactions in the gas phase were investigated, using FTIR spectroscopy. There have been many classical studies of exchange reactions of this sort in solution, principally using NMR spectroscopy (reviewed in Chapter 7). For completeness and to aid in the identification of the pyrolysis products later, the ¹H NMR spectra of mixtures of TMGa with TEGa, TIPGa, and TIBGa were investigated in d₈-toluene solution.
Figure 3.3: FTIR spectra of a mixture of SF$_6$ (10 torr) and TMGa (2 torr), before (A) and after (B) irradiation at 4 W of laser power for 120 s. Features marked are assigned as follows: (●) = SF$_6$, (□) = TMGa, and (○) = CH$_4$. The broad background feature centred around 1500 cm$^{-1}$ is a feature of TMGa pyrolysis, and is probably due to material deposited on the windows.
### TABLE 3.2: FTIR SPECTRA OF TRIETHYLGALLANE AND DIETHYLGALLANE (cm⁻¹).

<table>
<thead>
<tr>
<th>Et₃Ga (vapour)</th>
<th>Et₂GaH (liquid)</th>
<th>Et₂GaH (solid)</th>
<th>ASSIGNMENT</th>
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</thead>
<tbody>
<tr>
<td>2953 (s)</td>
<td>2947 (s)</td>
<td>2944 (s)</td>
<td>ν₉as,s(C-H)</td>
</tr>
<tr>
<td>2917 (s)</td>
<td>2904 (s)</td>
<td>2902 (s)</td>
<td></td>
</tr>
<tr>
<td>2882 (s)</td>
<td>2869 (s)</td>
<td>2867 (s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2814 (w)</td>
<td>2813 (w)</td>
<td>Overtones</td>
</tr>
<tr>
<td>2745 (w)</td>
<td>2731 (vw)</td>
<td>2730 (vw)</td>
<td>Overtones</td>
</tr>
<tr>
<td></td>
<td>1647 (s,br)</td>
<td>1657 (s,br)</td>
<td>ν₉as(Ga-H)</td>
</tr>
<tr>
<td>1467 (m)</td>
<td>1463 (m)</td>
<td>1462 (m)</td>
<td>δ₉as(CH₃)</td>
</tr>
<tr>
<td>1418 (w)</td>
<td>1419 (m)</td>
<td>1417 (w)</td>
<td>δ₉(CH₂)</td>
</tr>
<tr>
<td>1382 (w)</td>
<td>1377 (m)</td>
<td>1375 (w)</td>
<td>δ₉(CH₃)</td>
</tr>
<tr>
<td>1235 (w)</td>
<td>1231 (w)</td>
<td>1231 (sh)</td>
<td></td>
</tr>
<tr>
<td>1210 (w)</td>
<td>1189 (m)</td>
<td>1191 (m)</td>
<td>ω(CH₂)</td>
</tr>
<tr>
<td>1002 (w)</td>
<td>998 (m)</td>
<td>999 (m)</td>
<td>ρ(CH₃)</td>
</tr>
<tr>
<td>960 (w)</td>
<td>961 (sh)</td>
<td>961 (m)</td>
<td>ν(C-C)</td>
</tr>
<tr>
<td></td>
<td>937 (m)</td>
<td>938 (m)</td>
<td>ν(C-C)</td>
</tr>
<tr>
<td></td>
<td>817 (w,br)</td>
<td></td>
<td>ν₉s(Ga-H)</td>
</tr>
<tr>
<td></td>
<td>697 (sh)</td>
<td>698 (sh)</td>
<td>ρ(CH₂)</td>
</tr>
<tr>
<td>651 (m)</td>
<td>662 (m)</td>
<td>663 (m)</td>
<td>ρ(CH₂)</td>
</tr>
<tr>
<td>545 (m)</td>
<td>560 (m)</td>
<td>563 (mw)</td>
<td>ν₉as(Ga-C)</td>
</tr>
<tr>
<td>#</td>
<td>509 (m)</td>
<td>513 (mw)</td>
<td>ν₉s(Ga-C)</td>
</tr>
</tbody>
</table>

* Not allowed for monomeric Et₃Ga.
* References [12,23].
TABLE 3.3: FTIR SPECTRUM OF TRIMETHYLGALLANE (cm$^{-1}$).

<table>
<thead>
<tr>
<th>FTIR</th>
<th>REF.[24]</th>
<th>ASSIGNMENT#</th>
</tr>
</thead>
<tbody>
<tr>
<td>3055 (sh)</td>
<td>3053 (sh)</td>
<td>-</td>
</tr>
<tr>
<td>3002 (s)</td>
<td>3002 (s)</td>
<td>$\nu_{as}(\text{CH}_3)$</td>
</tr>
<tr>
<td>2919 (s)</td>
<td>2919 (s)</td>
<td>$\nu_{as}(\text{CH}<em>3) + \nu</em>{s}(\text{CH}_3)$</td>
</tr>
<tr>
<td>2869 (sh)</td>
<td>2850 (sh)</td>
<td>$2\delta_{as}(\text{CH}_3)$</td>
</tr>
<tr>
<td>1786 (vw)</td>
<td>1786 (vw)</td>
<td>$\nu_{as}(\text{GaC}<em>3) + \delta</em>{s}(\text{CH}_3)$</td>
</tr>
<tr>
<td>1733 (vw)</td>
<td>1732 (vw)</td>
<td>$\nu_{s}(\text{GaC}<em>3) + \delta</em>{s}(\text{CH}_3)$</td>
</tr>
<tr>
<td>1358 (w)</td>
<td>1255 (w)</td>
<td>-</td>
</tr>
<tr>
<td>1205 (m)</td>
<td>1205 (m)</td>
<td>$\delta_{s}(\text{CH}_3)$</td>
</tr>
<tr>
<td>772 (vs)</td>
<td>774 (vs)</td>
<td>$\rho(\text{CH}_3)$</td>
</tr>
<tr>
<td>726 (s)</td>
<td>725 (s)</td>
<td>$\rho(\text{CH}_3)$</td>
</tr>
<tr>
<td>584 (vs)</td>
<td>584 (vs)</td>
<td>$\nu_{as}(\text{GaC}_3)$</td>
</tr>
<tr>
<td>571 (vs)</td>
<td>571 (vs)</td>
<td>$\nu_{as}(\text{GaC}_3)$</td>
</tr>
</tbody>
</table>

# Assignments are those of reference [24].
TABLE 3.4: FTIR SPECTRUM OF TRIMETHYLAMINE (cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>FTIR</th>
<th>REF.[25]</th>
<th>ASSIGNMENT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2991 (sh)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2979 (sh)</td>
<td>2978</td>
<td>(\nu_{as}(C-H))</td>
</tr>
<tr>
<td>2965 (ms)</td>
<td>2970</td>
<td>(\nu_{as}(C-H))</td>
</tr>
<tr>
<td>2874 (w)</td>
<td>2872</td>
<td>(\nu_{s}(C-H))</td>
</tr>
<tr>
<td>2823 (s)</td>
<td>2822</td>
<td>(\nu_{s}(C-H))</td>
</tr>
<tr>
<td>2775 (vs)</td>
<td>2774</td>
<td>(\nu_{s}(C-H))</td>
</tr>
<tr>
<td>2737 (w)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1478 (m)</td>
<td>1478</td>
<td>(\delta_{as}(CH_3))</td>
</tr>
<tr>
<td>1466 (w)</td>
<td>1466</td>
<td>(\delta_{as}(CH_3))</td>
</tr>
<tr>
<td>1459 (m)</td>
<td>1459</td>
<td>(\delta_{as}(CH_3))</td>
</tr>
<tr>
<td>1453 (m)</td>
<td>1452</td>
<td>(\delta_{s}(CH_3))</td>
</tr>
<tr>
<td>1443 (m)</td>
<td>1444</td>
<td>(\delta_{s}(CH_3))</td>
</tr>
<tr>
<td>1397 (vw)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1275 (mw)</td>
<td>1273</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>1183 (m)</td>
<td>1183</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>1103 (w)</td>
<td>1102</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>1043 (m)</td>
<td>1043</td>
<td>(\nu(C-N))</td>
</tr>
<tr>
<td>826 (m)</td>
<td>825</td>
<td>(\nu(C-N))</td>
</tr>
</tbody>
</table>

* Assignments are those of reference [25].
3.4.2 FTIR Study of TMGa + TEGa Mixtures

Figure 3.4 shows computer added pre-recorded TEGa and TMGa IR spectra in the ratio 1:1, together with that of an equimolar mixture of the two. Within the time of mixing and acquisition of IR spectra (1-2 minutes), exchange reactions have already reached equilibrium, and no further detectable change takes place. Along with the bands attributable to TMGa and TEGa, there are new features, presumably due to Et2MeGa and Me2EtGa species. Although a detailed analysis of this spectrum has not been carried out, the significant differences are in the CH3 rocking region (700-800 cm⁻¹), and the ethyl CH2 rocking (650-750 cm⁻¹) vibrations. However, the clearest evidence for exchange reactions comes from the asymmetric Ga-C3 stretching vibrations (500-600 cm⁻¹); here the only clearly defined band observable in the mixture (567 cm⁻¹) lies between those of TMGa (doublet at 578 + 584 cm⁻¹) and TEGa (545 cm⁻¹).

3.4.3 1H NMR Study of TMGa + TEGa Mixtures

The 1H NMR spectra of the TEGa - I - TMGa mixture in d₈-toluene solution were uninformative, yielding spectra indistinguishable from those of the initial components even at 191 K. These results parallel those found for Me₂EtAl and Me₂EtIn systems in solution [8], and confirm the existence of very rapid Me-Et exchange processes.

3.4.4 1H NMR Study of TMGa - TEGa - NMe3 Adducts

Trimethylamine, NMe3, was added to the 1:1 gas phase mixture, dissolved in d₈-toluene, in order to slow down the alkyl exchange. The addition of Lewis bases to solve this problem is well documented in the literature and in our own work [12,13,26] and indeed the 1H NMR spectra of the NMe3 adducts revealed the presence of four species in a 1:3:3:1 ratio. These were identified as Et3Ga.NMe3, Et2MeGa.NMe3, EtMe2Ga.NMe3 and Me3Ga.NMe3; these species showed no
Figure 3.4: FTIR spectra of computer co-added spectra of TEGa and TMGa (A) and of a 1:1 mixture of the two (B). Note the changes in the region of the Ga-C stretching vibrations near 560 cm$^{-1}$. 
indication of exchange broadening even at room temperature. Table 3.5 lists $^1$H NMR data for the above adducts.

3.4.5 $^1$H NMR Study of TMGa + TIPGa - NMe$_3$ Adducts

The following species were clearly identified: $^3$Pr$_2$Ga.NMe$_3$, $^2$Pr$_2$MeGa.NMe$_3$, $^3$PrMe$_2$Ga.NMe$_3$, and Me$_3$Ga.NMe$_3$. In this case the changes in chemical shift of both Me and $^3$Pr protons were considerably more pronounced than in the ethyl series; this is attributed to steric effects.

3.4.6 TMGa + TIBGa Mixtures

In this system there was no evidence for exchange between TMGa and TIBGa in either the gas phase FTIR spectra of the native mixture or $^1$H NMR spectra of NMe$_3$ adducts. Evidently, Me and $^3$Bu groups do not undergo exchange and this is in agreement with the work of Cleaver and Barron for the Me and $^3$Bu system, where it proved possible to isolate the mixed alkyl species, $^3$Bu$_2$MeGa and $^3$BuMe$_2$Ga [9].

3.5 IR LPHP of TMGa + TEGa Mixtures

3.5.1 FTIR Study

IR LPHP experiments on TMGa + TEGa/SF$_6$ mixtures were carried out at a laser power of 2 watts, corresponding to an estimated maximum cell temperature of 550 K, according to Atiya [22]. This laser power is sufficient to lead to $\beta$-elimination in TEGa, but not to bring about reaction of TMGa alone [21]. Figure 3.5 shows the FTIR spectrum of a mixture of TMGa (5 torr), TEGa (5 torr) and SF$_6$ (10 torr), both before (A) and after (B) extended exposure to 2 watts of CO$_2$ laser radiation for 300 seconds.

Initially after a short period of pyrolysis, a viscous condensate formed on the cell walls and this was accompanied by a strong broad absorption at around 1650 cm$^{-1}$. This was identified from earlier work [12] as the asymmetric Ga-H-Ga stretch in
<table>
<thead>
<tr>
<th>Temperature</th>
<th>ASSIGNMENT</th>
<th>COUPLING</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K</td>
<td>(i) Ga-CH₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.30 (s)</td>
<td>-0.10 (s)</td>
</tr>
<tr>
<td></td>
<td>-0.33 (s)</td>
<td>-0.14 (s)</td>
</tr>
<tr>
<td></td>
<td>-0.35 (s)</td>
<td>-0.17 (s)</td>
</tr>
<tr>
<td></td>
<td>-0.38 (s)</td>
<td>-0.17 (s)</td>
</tr>
<tr>
<td></td>
<td>-0.44 (s)</td>
<td>-0.26 (s)</td>
</tr>
<tr>
<td></td>
<td>-0.23 (s)</td>
<td>-0.04 (d)</td>
</tr>
<tr>
<td></td>
<td>-0.25 (s)</td>
<td>-0.06 (d)</td>
</tr>
<tr>
<td></td>
<td>-0.15 (s)</td>
<td>0.03 (t)</td>
</tr>
<tr>
<td>203 K#</td>
<td>(i) Ga-CH₃</td>
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<tr>
<td></td>
<td>-0.04 (q)</td>
<td>0.52 (q)</td>
</tr>
<tr>
<td></td>
<td>0.36 (q)</td>
<td>0.49 (q)</td>
</tr>
<tr>
<td></td>
<td>0.35 (q)</td>
<td>0.49 (q)</td>
</tr>
<tr>
<td></td>
<td>0.45 (q)</td>
<td>0.57 (dq)</td>
</tr>
<tr>
<td></td>
<td>0.43 (q)</td>
<td>0.56 (dq)</td>
</tr>
<tr>
<td></td>
<td>0.52 (q)</td>
<td>0.65 (tq)</td>
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<tr>
<td></td>
<td></td>
<td>(ii) Ga-CH₂CH₃</td>
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<tr>
<td></td>
<td></td>
<td>J(CH₂CH₃)=7.8-8.0 Hz</td>
</tr>
<tr>
<td></td>
<td>(iii) Ga-CH(CH₃)₂ all septets,</td>
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<td></td>
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<td>J(CH(CH₃)₂)=7.6 Hz</td>
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<td>(iv) Ga-H</td>
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<td>4.85</td>
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<td>(s,br)</td>
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<td></td>
<td>1.81</td>
<td>1.73-1.54</td>
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* s=singlet, d=doublet, t=triplet, q=quartet; br=broad.
# Chemical shifts were either measured directly or extrapolated to 203 K.
Figure 3.5: FTIR spectra of the products of the IR LPHP of a mixture of SF$_6$ (10 torr), TMGa (5 torr) and TEGa (5 torr), before (A) and after (B) exposure to 2 W of laser power for 300 s. Features assigned to SF$_6$ (○), C$_2$H$_4$ (●), and Me$_2$GaH (●) are indicated.
diethylgallane. Sharp features due to ethene were also observed at 2989, 1889, and 949 cm$^{-1}$. As the reaction proceeded further increases in the ethene signals were observed, and the diethylgallane features decreased to be replaced by new peaks at 1288 and 1180 cm$^{-1}$. These are assigned to the stable dimeric form of dimethylgallane, Me$_2$Ga(\(\mu\)-H)$_2$GaMe$_2$, identified by Baxter et al. [27]. At no stage during the reaction was any methane formed or gallium metal deposited. It did not prove possible to eliminate all of the Ga-bound ethyl groups in one single pyrolysis step; this was only achieved after the rapid pumping away of ethene and SF$_6$, followed by addition of SF$_6$ and further pyrolysis, thus driving the system towards dimethylgallanes and monomethylgallane. Evidently, in this system $\beta$-elimination is reversible; this phenomenon is well known in Al systems, and the ease of insertion of ethene into Ga-H bonds was demonstrated by Pulham et al. in their synthesis of Et$_2$GaH [23].

3.5.2 $^1$H NMR Study

Following irradiation for approximately 36 minutes at 2 watts of power in total, the reaction cell was cooled to 77 K and pumped to remove ethene and SF$_6$. The remaining contents of the cell were then rapidly condensed into an NMR tube at 77 K. The solvent d$_8$-toluene was out-gassed at 77 K and then distilled into the tube at the same temperature.

The $^1$H NMR spectrum of the pyrolysis products was very complex. Figure 3.6A shows at 207 K, the presence of at least five broad Ga-H peaks at 2.77, 2.79, 2.84, 2.86, and 2.95 ppm respectively. The methyl group resonances fall into two sets, a broad singlet at $\delta^H$ -0.17 ppm, similar to that observed for the unpyrolysed mixture and assigned to the trialkylgallanes, and a complex group set between $\delta^H$ 0.00 and $\delta^H$ 0.20 ppm attributable to methyl gallium hydrides, shown in figure 3.6B. Similarly, the ethyl CH$_2$ resonances appear as an isolated quartet at $\delta^H$ 0.30 ppm arising from trialkylgallanes, and a complex overlapped cluster near $\delta^H$ 0.70 ppm.
Figure 3.6: $^1$H NMR spectrum of the pyrolysis products of the IR LPHP of TEGa and TMGa at 196 K. Only the regions of Ga-H (A) and Ga-CH$_3$ (B) resonances are shown, with features arising from Me$_6$Ga$_3$H$_3$ (●) and Me$_5$EtGa$_3$H$_3$ (■) identified. Weaker features arise from more highly ethylated species.
arising from ethyl gallium hydrides. The \( \text{CH}_3 \) fragments of the ethyl groups (\( \delta_H 1.24-1.33 \) ppm) are overlapped for all species reflecting the relative insensitivity of this group to variation at the gallium centre. Simultaneous high power homonuclear decoupling of all hydride resonances resulted in a pronounced sharpening of the Ga-\( \text{CH}_3 \) and ethyl \( \text{CH}_2 \) features, confirming the origin of these peaks and indicating a \( ^3J(\text{H-Ga-C-H}) \) smaller than the line width (0.5 Hz). Examination of these patterns reveal at least ten methyl resonances and broad unresolved ethyl \( \text{CH}_2 \) peaks. The most intense of the methyl resonances corresponds to dimethylgallane [27] (\( \delta_H 0.06 \) ppm) and can be matched to the strong isolated hydride peak at \( \delta_H 2.95 \) ppm. The origin of the rest of the species relies on the fact that dialkylgallanes exist in solution as trimers or higher units, \( \text{R}_{2n}^2 \text{GaH}_n \). Exchange of Me and Et groups is very rapid, and due to the higher ratio of Me to Et groups, the dominant species will therefore be \( \text{Me}_{2n}^2 \text{GaH}_n \), followed by \( \text{Me}_{2n-1}^2 \text{EtGaH}_n \) and \( \text{Me}_{2n-2}^2 \text{Et}_2 \text{GaH}_n \), with negligible contributions from more highly ethylated species. Figure 3.7 shows the resulting stereochemical consequences when \( n=3 \). The dominant species (A) will exhibit 3 Me resonances in the ratio 1:2:2, (I) in figure 3.7. The remaining weaker resonances arise from the disubstituted species B, C and D. Association into forms other than trimers would lead to different patterns being observed.

At room temperature all hydride, methyl and ethyl resonances collapsed into single features. Integration of this spectrum provided an estimate of relative Me:hydride:Et in the ratio 5:1.5:1 in the products, suggesting a substantial loss of ethyl and/or hydride units at some stage (\( \text{H}_2 \)), a sharp singlet at \( \delta_H 4.50 \) ppm was observed in this spectrum, similar to that produced by the disproportionation of monoethylgallane in the work of triethylgallane [12]).

3.6 Adduct Formation with NMe\(_3\)

3.6.1 FTIR Study

From our studies of the IR LPHP of TEGa [12], TIBGa, TTBGa [13], and
Figure 3.7: Ga-Me and Ga-H environments in Me$_5$EtGa$_2$H$_3$ (A) and Me$_4$Et$_2$Ga$_3$H$_3$ (B = gem diethyl, C = cis diethyl, and D = trans diethyl). The Ga$_3$H$_3$ ring is assumed to be planar in each case.
TIPGa [28], the identification of the species present is greatly facilitated by the formation of monomeric NMe$_3$ adducts in the vapour phase. Figure 3.8 shows the addition of excess NMe$_3$ to the pyrolysis products. This results in the broad Ga-H asymmetric stretch of Et$_2$GaH and the two Ga-H stretches of Me$_2$GaH, being replaced by a structured narrower band (1780-1860 cm$^{-1}$) in the region characteristic of terminal Ga-H stretches in NMe$_3$ adducts. In this feature several peaks may be clearly ascribed to being homoalkylated gallanes on comparison with those identified in AlH$_3$.NMe$_3$ mixtures with TEGa [29] and TMGa [30], or with the pyrolysis of TEGa alone [12]. They are: Me$_2$GaH.NMe$_3$ at 1814 cm$^{-1}$, MeGaH$_2$.NMe$_3$ at 1825 cm$^{-1}$, Et$_2$GaH.NMe$_3$ at 1798 cm$^{-1}$ (very weak), EtGaH$_2$.NMe$_3$ at 1820 cm$^{-1}$ (weak), and intermediate between the two homodialkylgallanes is an additional peak at 1807 cm$^{-1}$, which is assigned to the new species EtMeGaH.NMe$_3$. The two Ga-H deformation peaks characteristic of dialkylgallanes (820 cm$^{-1}$) and monoalkylgallanes (750 cm$^{-1}$) are also evident. More precise quantitative results were obtained from the $^1$H NMR spectra of the above mixture.

3.6.2 $^1$H NMR Study

After irradiation, excess NMe$_3$ was added to the pyrolysis cell and the volatile products were condensed into an NMR tube at 77 K, followed by the addition of degassed d$_8$-toluene. Figure 3.9 shows the $^1$H NMR spectrum of the Ga-CH$_3$ resonances of the NMe$_3$ adducts at 191 K. At this temperature the features of all the species in the mixture are clearly resolved and easily identified. The Ga-CH$_3$ resonances are diagnostic for the number of Ga-H groups and reveal the $^3$J(H-Ga-C-H) coupling hitherto reported for only ethylgallane trimethylamine adducts [12]. The singlet trialkylgallane adduct resonances are identical with those reported above for the pre-pyrolysis mixtures. Two doublets may be identified as Me$_2$GaH.NMe$_3$ [$\delta_H$ -0.03 ppm, $^3$J(H-Ga-C-H) = 1.6 Hz] and MeEtGaH.NMe$_3$ [$\delta_H$ -0.05 ppm, $^3$J(H-Ga-C-H) = 1.6 Hz], and a triplet due to MeGaH$_2$.NMe$_3$
Figure 3.8: FTIR spectrum of the terminal Ga-H stretching vibrations apparent on addition of NMe₃ to the pyrolysis products of figure 3.5. Features identified arise from MeGaH₂·NMe₃ (●), EtGaH₂·NMe₃ (○), Me₂GaH·NMe₃ (●), and MeEtGaH·NMe₃ (▲). That arising from Et₂GaH·NMe₃ is indetectable, and the feature near 1845 cm⁻¹ (○) probably arises from GaH₃·NMe₃.
Figure 3.9: $^1$H NMR spectrum of the methyl resonances of the trimethylamine adducts at 191 K. Singlets arise from $\text{Me}_3\text{Ga.NMe}_3$ (1), $\text{Me}_2\text{Et.Ga.NMe}_3$ (2), and $\text{MeEt}_2\text{Ga.NMe}_3$ (3), doublets from $\text{Me}_2\text{GaH.NMe}_3$ (4) and $\text{MeEtGaH.NMe}_3$ (5), and the triplet from $\text{MeGaH}_2\cdot\text{NMe}_3$ (6).
[δH 0.03 ppm, J(H-Ga-C-H)=1.9 Hz]. Similar assignments have been made in the ethyl CH2, see table 3.5, where the H-Ga-C-H splitting is only 1.1 Hz. The hydride resonances are near δH 5.00 ppm, are broad and overlapped, with three signals observed for samples in which the ethyl groups have not been fully depleted. Upon slow warming of the sample to room temperature all the hydride resonances collapse into one very broad signal, and at the same time all coupling to Ga-H protons disappears. However, all the Me and Et resonances remain well resolved, indicating little tendency to undergo alkyl group exchange at this temperature, and this actually makes the identification of the ethyl group CH2 resonances easier than at low temperature. Figure 3.10 illustrates the 1H NMR spectrum of the ethyl group CH2 resonances at 191 and 298 K.

3.7 Discussion and Conclusions

The FTIR and 1H NMR observations show clearly that exchange of Me groups with either Et or iPr groups occurs rapidly in the gas phase, whereas exchange of Me groups with iBu (or tBu [9]) does not occur. The most likely gas phase mechanism for exchange is metathesis via transient bridged dimers or higher oligomers, for example

\[ R_3\text{Ga} + R'_3\text{Ga} \leftrightarrow R_2\text{Ga}R\{R\}R\{R'\}R_2\text{Ga}R' \leftrightarrow R_2R'R'\text{Ga} + R'R\text{Ga} \quad [3.26] \]

Exchange is only thought to be favourable for alkyl groups which have a tendency towards bridge formation, which is directly related to steric size in that \( \text{Me}>\text{Et}>\text{iPr}>\text{iBu}>\text{tBu} \), and also due to the fact that the corresponding trialkylalananes dimerize; it is therefore expected that trialkylgallanes will undergo exchange reactions.

The IR LPHP studies of the TMGa + TEGa mixtures are very revealing, both in their own right and in the additional light they shed on the TEGa system. The products identified are entirely consistent with the exchange of alkyl groups, coupled with the loss of Ga-Et groups via β-hydride elimination and the total retention of Ga-Me groups at the temperatures used, as illustrated in figure 3.11. The laser pyrolysis of TMGa + TEGa has provided a novel route to the production of
Figure 3.10: $^1$H NMR spectra of the pyrolysis products of TEGa and TMGa mixtures with NMe$_3$ at 222 K (A) and 298 K (B). Only the region of the Ga-CH$_2$CH$_3$ protons is shown. In figure (A) the following features are identified: (●) = Et$_3$Ga.NMe$_3$ + Et$_2$MeGa.NMe$_3$ + EtMe$_2$Ga.NMe$_3$, (●) = MeEtGaH.NMe$_3$, (●) = Et$_2$GaH.NMe$_3$, and (●) = EtGaH$_2$.NMe$_3$. In figure (B) the above species are less overlapped and can be identified as follows: (1) = Me$_2$EtGa.NMe$_3$, (2) = MeEt$_2$Ga.NMe$_3$, (3) = MeEtGaH.NMe$_3$, (4) = Et$_2$GaH.NMe$_3$, and (5) = EtGaH$_2$.NMe$_3$. 
Figure 3.11: Reaction scheme to show the production of the observed products in the pyrolysis mixtures of TEGa and TMGa.
dialkylgallanes, in particular dimethylgallane, which was synthesized and characterized by Baxter et al. [27]. These workers reduced trimethylgallane using sodium tetrahydridogallate, which is itself prepared from gallium (III) chloride and sodium hydride, in diethyl ether at room temperature, to produce dimethylgallane. This was shown to be dimeric in the vapour phase, from mass spectrometric evidence, and confirmed our observations.

As in the TEGa study by Grady [12], the formation of adducts with trimethylamine enabled all the products to be identified fully conclusively in both the FTIR and $^1$H NMR studies. Most important of all was the observation of the previously undetected monomethylgallane in this system.

The predominance of the $\beta$-hydride elimination mechanism as the sole mode of decomposition in this mixture is entirely in accordance with both the experimentally determined (175-195 kJ mol$^{-1}$ for TEGa [20,31,32], 249 kJ mol$^{-1}$ for TMGa [16]) and calculated (184 kJ mol$^{-1}$ for $\beta$-hydride elimination, 251 kJ mol$^{-1}$ for bond homolysis [33]) activation energies for the two possible processes. On the other hand, these observations run counter to those of the photolysis of $^1$Bu$_2$MeGa and $^1$BuMe$_2$Ga, where mass spectrometric evidence suggested that $\beta$-hydride elimination occurs only after the loss of an alkyl radical [11]. The origin of this difference is not clear.

The TEGa + TMGa mixture study presented does, however, cast doubt on the viability of mixed alkyl group systems as precursors for MOVPE, since the change in constitution as the reaction proceeds is likely to result not only in a non-uniform layer thickness, but also a graduation in carbon content. These factors are additional to any preferential volatilisation of lighter components. However, growth studies using mixtures of TMGa and TEGa have yet to be carried out. It is important that the differences in conditions between the gas phase homogeneous pyrolysis of TEGa and TMGa mixtures described in this chapter and those in an MOVPE growth reactor are taken into account, as surface reactions play a significant role in the latter system with
the possible consequence that the $\beta$-hydride elimination mechanism may be less predominant.

Future work on this system is to be carried out to compare the differences in the yield of radicals between the laser pyrolysis and the hot-tube pyrolysis using ESR matrix isolation [34].
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unpublished observations.
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N. P. Fatyushia, V. V. Gavrilenko, Yu. S. Dementov, A. G. Petrik and


[34] G. P. Mills and A. D. Workman, personal communication.
Chapter Four

IR LPHP of Triisopropylgallane, Triisobutylgallane, and Tri-tert-butylgallane
4.1 Introduction

In this chapter the gas phase pyrolysis of TIPGa, triisopropylgallane, TIBGa, triisobutylgallane, and TTBGa, tri-tert-butylgallane have been studied using infrared laser powered homogeneous pyrolysis. The aims of this study were firstly to examine the major decomposition pathway in these sterically hindered systems, and secondly to compare the results with the successful study of TEGa by Grady [1]; most importantly, however, these three compounds are currently being investigated as potential low temperature sources for gallium deposition [2,3].

The pyrolysis products were identified by FTIR and $^1$H NMR spectroscopy, and this confirmed that the predominant reaction pathway is $\beta$-hydride elimination in all cases, but that the pyrolysers proceed at significantly lower temperatures than TEGa. Further clarification of the reaction products was achieved by the addition of trimethylamine, which forms well documented adducts with organogallium compounds as shown in Chapter 3.

This chapter begins with a review of previous work which has been carried out on higher trialkylgallanes and alanes, followed by the results obtained and finally the discussion and conclusions reached. Some of the work presented in this chapter is described in J. Mater. Chem., 1992, 2, 539.

4.2 Review

The mechanism of decomposition of the higher trialkyls of gallium has not been extensively studied. However, the thermal decomposition of tri-n-propylgallane has been carried out by Aleksandrov et al. [4]. These workers pyrolysed tri-n-propylgallane in the temperature range 473-553 K and the gaseous reaction products were analysed by mass spectrometry. The major products were propene and $H_2$; a small amount of propane was also detected. From the results these workers concluded that the mode of decomposition was $\beta$-hydride elimination, with the instantaneous decomposition of the hydride to gallium metal, $H_2$, and propene.
Aleksandrov and co-workers also studied the thermal decomposition of tri-tert-butylgallane, in the same temperature range and for this system also, they concluded that \( \beta \)-hydride elimination was the predominant pathway, producing isobutene and \( H_2 \).

Travkin et al. [5] pyrolysed both tri-tert-butylgallane and triisobutylgallane in the temperature range 473-773 K, using differential thermal analysis (DTA) and the major hydrocarbon products analysed by gas chromatography were butane and isobutane respectively. A free radical mechanism was proposed.

The pyrolysis of triisobutylalane at 525 K was reported by Ziegler et al. [6] in 1960. Analysis of the gas phase products revealed isobutene and \( H_2 \) to be the major components. Bent and co-workers used this facile \( \beta \)-elimination of isobutene to successfully grow high purity Al layers [7]. In this study they proposed two surface mechanisms, based on the analysis of the gaseous reaction products by mass spectrometry. They are as follows:

i) \( \beta \)-hydride elimination - this dominates at surface temperatures below 600 K and leads to carbon free, crystalline Al films:

\[
\begin{align*}
{^i}_{Bu_3}Al & \rightarrow {^i}_{Bu_2}AlH + (CH_3)_2C=CH_2 \\
{^i}_{Bu_2}AlH & \rightarrow 2(CH_3)_2C=CH_2 + H_2 + Al
\end{align*}
\]  

ii) \( \beta \)-methyl elimination - dominates at surface temperatures above 600 K and leads to carbon incorporation into Al films:

\[
{^i}_{Bu_3}Al \rightarrow {^i}_{Bu_2}AlMe + CH_3CH=CH_2
\]
4.3 Experimental

Chemicals

The purification and handling of the samples used for the IR LPHP of TIPGa, TIBGa, and TTBGa have been described in Chapter 2. The purities of all the compounds were checked using FTIR and $^1$H NMR spectroscopy. Tables 4.1, 4.2, and 4.3 report the IR spectra of TIPGa, TIBGa and TTBGa respectively, and table 3.4 reports the IR spectrum of NMe$_3$.

Apparatus

The equipment used has been described fully in Chapter 2. The vapour pressures of TIPGa, TIBGa and TTBGa are relatively low (ca. 0.20 torr at room temperature), and the reaction products are also comparatively involatile. For this reason the cell shown in figure 2.2 was used in these experiments. The reaction cell was cooled to 77 K and the species involved was condensed into the hollow of the cell. In all experiments 10 torr of SF$_6$ was used.

4.4 IR LPHP of TIPGa

4.4.1 FTIR Study

IR LPHP experiments on TIPGa/SF$_6$ mixtures were carried out at laser powers ranging from 1.13 to 3.80 Watts. According to the work of Atiya [12], these laser powers correspond to maximum cell temperatures of between 500-630 K. Figure 4.1 shows the FTIR spectrum of a mixture of SF$_6$ (10 torr) and TIPGa (as liquid in the cell), both before (A) and after (B), exposure to 2.03 Watts of CO$_2$ laser radiation for 270 seconds. From the FTIR study the major observable pyrolysis product was propene, which has characteristic vibrations at 2979, 2916, 1650, 1448, and 913 cm$^{-1}$. During the course of the pyrolysis an extremely viscous liquid began to form on the walls of the cell. This corresponded to the appearance of a new broad peak centred at 1618 cm$^{-1}$. This absorption was somewhat obscured by the strong propene peak at 1650 cm$^{-1}$; therefore the cell was cooled down to 77 K and volatile materials
TABLE 4.1: FTIR SPECTRA OF TRIISOPROPYLGALLANE AND DIISOPROPYLGALLANE (cm$^{-1}$).

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* Liquid phase spectrum.
# Liquid/solid phase spectrum.
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<td>1170 (w,sh)</td>
<td>–</td>
<td>$\rho(\text{CH}_2)$</td>
</tr>
<tr>
<td>1157 (m)</td>
<td>1160 (m)</td>
<td>1160 (m)</td>
<td>$\rho(\text{CH}_2)$</td>
</tr>
<tr>
<td>1073 (m)</td>
<td>1076 (m)</td>
<td>1077 (m)</td>
<td>?</td>
</tr>
<tr>
<td>1013 (m)</td>
<td>1017 (m)</td>
<td>1019 (m)</td>
<td>$\nu_{as}(\text{C-C})$</td>
</tr>
<tr>
<td>813 (w)</td>
<td>812 (w)</td>
<td>810 (w)</td>
<td>$\nu_s(\text{C-C})$</td>
</tr>
<tr>
<td>–</td>
<td>715 (m,br)</td>
<td>715 (m,br)</td>
<td>$\nu_s(\text{Ga-H})$</td>
</tr>
<tr>
<td>615 (w)</td>
<td>636 (w)</td>
<td>–</td>
<td>$\nu_{as}(\text{Ga-C})$</td>
</tr>
</tbody>
</table>

# Based on spectra of diethylgallane [1] and triisobutylgallane [10].
TABLE 4.3: FTIR SPECTRA OF TRI-TERT-BUTYLGALLANE AND DI-TERT-BUTYLGALLANE (cm⁻¹).

<table>
<thead>
<tr>
<th>$t_{\text{Bu}_3\text{Ga}}$</th>
<th>$t_{\text{Bu}_2\text{GaH}}$</th>
<th>ASSIGNMENT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2954 (w,br)</td>
<td>2956 (m,sh)</td>
<td>$\nu_{\text{as}}(\text{CH}_3)$</td>
</tr>
<tr>
<td>2926 (w,br)</td>
<td>2927 (m)</td>
<td>$\nu_{\text{as}}(\text{CH}_3)$</td>
</tr>
<tr>
<td>2876 (w)</td>
<td>2869 (m,sh)</td>
<td>$\nu_{\text{s}}(\text{CH}_3)$</td>
</tr>
<tr>
<td>2841 (m)</td>
<td>2842 (s)</td>
<td>$\nu_{\text{s}}(\text{CH}_3)$</td>
</tr>
<tr>
<td>-</td>
<td>2706 (w)</td>
<td>Overtone</td>
</tr>
<tr>
<td>-</td>
<td>1530 (m,vbr)</td>
<td>$\nu_{\text{as}}(\text{Ga-H})$</td>
</tr>
<tr>
<td>1468 (m)</td>
<td>1468 (m)</td>
<td>$\delta_{\text{as}}(\text{CH}_3)$</td>
</tr>
<tr>
<td>-</td>
<td>1454 (m,sh)</td>
<td>$\delta_{\text{as}}(\text{CH}_3)$</td>
</tr>
<tr>
<td>1386 (w)</td>
<td>1386 (w)</td>
<td>$\delta_{\text{s}}(\text{CH}_3)$</td>
</tr>
<tr>
<td>1363 (m)</td>
<td>1362 (m)</td>
<td>$\delta_{\text{s}}(\text{CH}_3)$</td>
</tr>
<tr>
<td>1174 (w)</td>
<td>1189 (w)</td>
<td>$\nu(\text{CC}) + \delta(\text{CCH})$</td>
</tr>
<tr>
<td>-</td>
<td>1161 (m)</td>
<td>$\nu(\text{CC}) + \delta(\text{CCH})$</td>
</tr>
<tr>
<td>1014 (w)</td>
<td>1011 (w,sh)</td>
<td>$\nu(\text{CC}) + \delta(\text{CCH})$</td>
</tr>
<tr>
<td>1005 (w)</td>
<td>1005 (w)</td>
<td>$\nu(\text{CC}) + \delta(\text{CCH})$</td>
</tr>
<tr>
<td>937 (w)</td>
<td>944 (w)</td>
<td>$\rho(\text{CH}_3)$</td>
</tr>
<tr>
<td>805 (m)</td>
<td>805 (m)</td>
<td>$\nu_{\text{s}}(\text{C-C}_3)$</td>
</tr>
<tr>
<td>-</td>
<td>730 (m,br)</td>
<td>$\nu_{\text{s}}(\text{Ga-H})$</td>
</tr>
<tr>
<td>-</td>
<td>653 (m,br)</td>
<td>$\nu_{\text{s}}(\text{Ga-H})$</td>
</tr>
<tr>
<td>536 (w,br)</td>
<td>538 (vw,br)</td>
<td>$\nu_{\text{as}}(\text{Ga-C})$</td>
</tr>
</tbody>
</table>

Figure 4.1: FTIR spectra of a mixture of SF\textsubscript{6} (10 torr) and TIPGa (as liquid on the cell windows), before (A) and after (B) irradiation at 2 W of laser power for 270 s. Features marked are assigned as follows: (●) = SF\textsubscript{6}, (●) = C\textsubscript{3}H\textsubscript{6}, and (○) = \textsuperscript{1}Pr\textsubscript{2}GaH.
Figure 4.2: FTIR spectrum of $^1$Pr$_2$GaH (solid/liquid film) generated by the IR LPHP of $^1$Pr$_3$Ga. Note the bridging Ga-H vibrations are marked ●.
such as SF₆ and propene were pumped away. The cell was then gradually warmed up to room temperature, where the product proved to be an involatile crystalline solid, which melted at room temperature, but was readily soluble in the starting material, TIPGa. Figure 4.2 shows the FTIR spectrum of this product condensed onto the cell windows, which was identified as diisopropylgallane, by comparison with the known spectra of Me₂GaH [13] and Et₂GaH [1]. The IR vibrations of ¹Pr₂GaH are listed in table 4.1.

It is also worthwhile commenting on the fact that, there was a considerable amount of gallium metal deposition in this system, in comparison with the TEGa, TIBGa and TTBGa systems. This observation, coupled with the relatively low yield of diisopropylgallane, led us to believe that a radical bond homolysis mechanism could be competing with the β-hydride elimination route. Thus the pyrolysis mechanism was investigated further by collecting the volatile reaction products, from a range of experiments at different laser powers, and NMR samples were prepared in d₈-toluene.

4.4.2 ¹H NMR Study

It did not prove possible to obtain a spectrum of diisopropylgallane using the techniques available as it was too involatile. Numerous attempts to secure a solution of the product in d₈-toluene resulted in the recovery of triisopropylgallane only. Instead greater emphasis was placed upon the analysis of the hydrocarbon products, using ¹H NMR spectroscopy.

At 1.13 watts, the pyrolysis products were propene and propane in the ratio 3:1. At laser powers above 1.50 watts, the radical recombination product 2,3-dimethylbutane was observed also, and was found to be in the ratio of 1:2.4 with propene. The appearance of propane can largely be attributed to the hydrolysis of the starting material during the condensation into the reaction cell, and then later into the NMR tube.
The full $^1H$ NMR spectra at 298 K in $d_8$-toluene consisted of the following:

i) Propane

$$CH_3CH_2CH_3 - \delta_H 0.87 \text{ ppm, } t;$$
$$CH_3CH_2CH_3 - \delta_H 1.05 \text{ ppm, complex multiplet.}$$

ii) Propene

$$(CH_3)CH=CH_2 - \delta_H 5.70 \text{ ppm, complex multiplet;}$$
$$(CH_3)CH=CH_2 - \delta_H 4.94 \text{ ppm, complex multiplet;}$$
$$(CH_3)CH=CH_2 - \delta_H 1.56 \text{ ppm, complex doublet.}$$

iii) 2,3-Dimethylbutane

$$\text{(CH}_3\text{)}_2\text{CHCH(CH}_3\text{)}_2 - \delta_H 0.81 \text{ ppm, d;}$$
$$\text{(CH}_3\text{)}_2\text{CHCH(CH}_3\text{)}_2 - \delta_H 1.33 \text{ ppm, complex multiplet.}$$

4.5 Adduct Formation with NMe$_3$

4.5.1 FTIR Study

As was shown in the work on TMGa + TEGa mixtures in Chapter 3, the formation of NMe$_3$ adducts can provide conclusive identification of the species involved. Addition of NMe$_3$ vapour to the isolated diisopropylgallane resulted in the FTIR spectrum shown in figure 4.3. Features attributable to both free diisopropylgallane ($\nu_{as}(\text{Ga-H})$ bridging at 1618 cm$^{-1}$, and $\nu_s(\text{Ga-H})$ at 652 cm$^{-1}$), and adducted diisopropylgallane ($\nu(\text{Ga-H})$ terminal at 1770 cm$^{-1}$ and $\delta(\text{Ga-H})$ at 740 cm$^{-1}$) were observed.

4.5.2 $^1H$ NMR Study

The contents of the cell from figure 4.3 were condensed into an NMR tube at 77 K and $d_8$-toluene was distilled into the tube at this temperature. Table 4.4 lists the $^1H$ NMR spectra recorded at 192, 236, and 298 K respectively and figure 4.4 shows representative spectra. At all temperatures the region of the septet $\text{Ga-CH(Ch}_3\text{)}_2$ resonances is overlapped for both $^1\text{Pr}_3\text{Ga.NMe}_3$ and $^1\text{Pr}_2\text{GaH.NMe}_3$, while for the
Figure 4.3: FTIR spectrum of a mixture of $^1$Pr$_2$GaH and $^1$Pr$_2$GaH.NMe$_3$. Features marked are identified as follows: (O) = Ga-H bridging bonds in $^1$Pr$_2$GaH and (●) = Ga-H terminal bonds in $^1$Pr$_2$GaH.NMe$_3$. 
**TABLE 4.4: $^1$H NMR CHEMICAL SHIFTS OF ISOPROPYLGALLANE TRIMETHYLAMINE ADDUCTS (ppm).**

<table>
<thead>
<tr>
<th>CHEMICAL SHIFT /ppm</th>
<th>298 K</th>
<th>236 K</th>
<th>192 K</th>
<th>ASSIGNMENT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Ga–CH(CH$_3$)$_2$#</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.85 (s)</td>
<td>0.90 (s)</td>
<td>0.95 (s)</td>
<td>[Ga$^i$Pr$_3$.NMe$_3$]</td>
<td></td>
</tr>
<tr>
<td>0.85 (s)</td>
<td>0.90 (s)</td>
<td>0.95 (s)</td>
<td>[Ga$^i$Pr$_2$.H.NMe$_3$]</td>
<td></td>
</tr>
<tr>
<td>(ii) Ga–CH(CH$_3$)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.39 (d)</td>
<td>1.50 (d)</td>
<td>1.59 (d)</td>
<td>[Ga$^i$Pr$_3$.NMe$_3$]</td>
<td></td>
</tr>
<tr>
<td>1.39 (d)</td>
<td>1.54 (d)</td>
<td>1.64 (d)</td>
<td>[Ga$^i$Pr$_2$.H.NMe$_3$]</td>
<td></td>
</tr>
<tr>
<td>(iii) Ga–H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>collapsed</td>
<td>4.71 (s,br)</td>
<td>4.81 (s)</td>
<td>[Ga$^i$Pr$_2$.H.NMe$_3$]</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>4.76 (s,br)</td>
<td>[Ga$^i$Pr$_2$.H.NMe$_3$]?</td>
<td></td>
</tr>
<tr>
<td>(iv) NMe$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.00 (s,br)</td>
<td>2.07 (s,br)</td>
<td>2.08 (s,br)</td>
<td>free NMe$_3$</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>1.66 (s,br)</td>
<td>1.53 (s,br)</td>
<td>complexed NMe$_3$</td>
<td></td>
</tr>
</tbody>
</table>

* $J[CH–(CH$_3$)$_2$]= 7.60 Hz in all cases.
# All septets.
? Tentative assignment.
Figure 4.4: $^1$H NMR spectra of $^i$Pr$_3$Ga.NMe$_3$ and $^i$Pr$_2$GaH.NMe$_3$ at 192 K, 236 K and 298 K. Features marked (●) arise from the Ga-CH(CH$_3$)$_2$ protons and (○) and (★) are ascribed to the Ga-CH(CH$_3$)$_3$ protons of $^i$Pr$_3$Ga.NMe$_3$ and $^i$Pr$_2$GaH.NMe$_3$ respectively. (★) is due to complexed NMe$_3$. 
Ga-CH(CH$_3$)$_2$ protons at 192 K and 236 K the two sets of doublets were clearly resolved. At 192 K the spectrum revealed the presence of a characteristically broad Ga-H resonance at $\delta_H$ 4.81 ppm attributed to $^i$Pr$_2$GaH.NMe$_3$. An additional weak peak at $\delta_H$ 4.76 ppm was also observed; this is tentatively assigned as $^i$PrGaH$_2$.NMe$_3$. Unlike the TEGa system [1], the J(Ga-H) splitting was too small to be detected in this case, continuing the trend in the size of the coupling constant observed for Me$_2$GaH.NMe$_3$, (J(Ga-H)=1.6 Hz) and Et$_2$GaH.NMe$_3$, (J(Ga-H)=1.1 Hz). Only at 192 K is complexed NMe$_3$ observed, above this temperature all the NMe$_3$ becomes unbound from the isopropylgallanes and this instability reflects the effectiveness of TIPGa as a growth precursor.

4.6 IR LPHP of TIBGa

4.6.1 FTIR Study

IR LPHP experiments on TIBGa/SF$_6$ mixtures were carried out at laser powers of between 1.25-3.20 watts, corresponding to estimated maximum cell temperatures in the region of 500-610 K [12]. Figure 4.5 shows the FTIR spectrum of an SF$_6$ (10 torr) and TIBGa (liquid film) mixture, both before (A) and after (B) exposure to 1.20 watts of radiation for 60 seconds. In this figure, (C) represents the pyrolysis product, a viscous liquid, after the removal of the volatile components by pumping out the cell at 77 K. This product proved to be diisobutylgallane; here the characteristic asymmetric stretch of the Ga-H-Ga bridging bond appears at 1650 cm$^{-1}$, somewhat higher than in diisopropylgallane, and a single symmetric hydride stretch at 700 cm$^{-1}$ is also observed. The IR vibrations of diisobutylgallane are listed in table 4.2, and they are almost identical with those reported by Markova et al. [9]. The only hydrocarbon pyrolysis product formed in this system was 2-methylpropene, with its characteristic peaks at 3087, 2945, 1665, 1459, 1382, and 890 cm$^{-1}$. At higher laser powers, identical pyrolysis products were formed, but under these conditions there was also a slight deposition of gallium onto the cell walls. However, most
Figure 4.5: FTIR spectra showing the formation of $^1$Bu$_2$GaH from the IR LPHP of $^1$Bu$_3$Ga, before (A) and after (B) exposure to 1.20 W of laser radiation for 60 s. Spectrum (C) is that of the pyrolysis product after removal of volatile components; note in particular the bridging Ga-H vibrations marked •.
importantly, at no time were any radical recombination products observed; even at 3.20 watts only butane and 2-methylpropene were formed in the approximate ratio of 1:3.75.

4.6.2 $^1$H NMR Study

The diisobutylgallane isolated in figure 4.5(C), was condensed into an NMR tube at 77 K and the solvent used was d$_8$-toluene. Table 4.5 lists the chemical shifts of the species recorded at 222 K. A broad Ga-H resonance at $\delta_H$ 3.14 ppm was observed and identified as diisobutylgallane (cf. 2.95 ppm for Me$_2$GaH and 2.85 ppm for Et$_2$GaH at the same temperature [14]). A number of clearly resolved doublets were also observed; on comparison with a pure sample of TIBGa these peaks were attributed to the (CH$_3$)$_2$CHCH$_2$Ga and the (CH$_3$)$_2$CHCH$_2$Ga protons in TIBGa and DIBGaH respectively. These resonances are illustrated in figure 4.6. Unfortunately the (CH$_3$)$_2$CHCH$_2$Ga protons in both species form a nonet, which was largely obscured by the CD$_3^-$-protonated impurity signal of the d$_8$-toluene. It must also be stressed that the resonances ascribed to $^1$BuGaH$_2$ are only tentative.

The $^1$H NMR spectra recorded at room temperature comprised of a strong doublet, as a result of the methyl resonances of all species collapsing due to the small differences in their respective chemical shifts. The -CH$_2$ resonances became very broad and unresolvable due to there being large differences in the chemical shifts of the three species.

4.7 Adduct Formation with NMe$_3$

4.7.1 FTIR Study

On addition of NMe$_3$, both hydride peaks shift in a similar manner to that observed in the TIPGa system. As shown in figure 4.7 the terminal Ga-H bond vibrations in $^1$Bu$_2$GaH,NMe$_3$ were recorded at 1782 and 725 cm$^{-1}$. 

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TABLE 4.5: $^1$H NMR CHEMICAL SHIFTS OF $^i$Bu$_3$Ga, $^i$Bu$_2$GaH AND $^i$BuGaH$_2$ (ppm) AT 222 K.

<table>
<thead>
<tr>
<th>CHEMICAL SHIFT/ppm</th>
<th>ASSIGNMENT</th>
<th>COUPLING/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Ga-CH$_2$CH(CH$_3$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.63 (d)</td>
<td>[Ga$^i$Bu$_3$]</td>
<td>J=7.10 Hz</td>
</tr>
<tr>
<td>0.98 (d)</td>
<td>[Ga$^i$Bu$_2$H]</td>
<td>J=7.15 Hz</td>
</tr>
<tr>
<td>1.21 (d,w)?</td>
<td>[Ga$^i$BuH$_2$]</td>
<td>J=6.40 Hz</td>
</tr>
<tr>
<td>(ii) Ga-CH$_2$CH(CH$_3$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.08 (d)</td>
<td>[Ga$^i$Bu$_3$]</td>
<td>J=6.50 Hz</td>
</tr>
<tr>
<td>1.14 (d)</td>
<td>[Ga$^i$Bu$_2$H]</td>
<td>J=6.50 Hz</td>
</tr>
<tr>
<td>1.34 (d,w)?</td>
<td>[Ga$^i$BuH$_2$]</td>
<td>J=6.20 Hz</td>
</tr>
<tr>
<td>(iii) Ga-CH$_2$CH(CH$_3$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.09 (nonet, overlapped with CD$_3$ in toluene)</td>
<td>[Ga$^i$Bu$_3$]</td>
<td>-</td>
</tr>
<tr>
<td>(iv) Ga-H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.14 (s,br)</td>
<td>[Ga$^i$Bu$_2$H]</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>[Ga$^i$BuH$_2$]</td>
<td></td>
</tr>
</tbody>
</table>

? Tentative assignment.

* J(Ga-H) was not measured.
Figure 4.6: $^1$H NMR spectrum of $^i$Bu$_3$Ga (■), $^i$Bu$_2$GaH (▲), and $^i$BuGaH$_2$ (●) at 222K, pyrolysis products from the IR LPHP of $^i$Bu$_3$Ga. Only the region of CH$_2$CH(CH$_3$)$_2$ and CH$_2$CH(CH$_3$)$_2$ protons is shown: doublets (arising from coupling to CH$_2$CH(CH$_3$)$_2$).

$\delta$ H/ppm
Figure 4.7: FTIR spectrum of Br₂Ga₂H₂NMe₃. Note the terminal Ga-H vibrations marked.
4.7.2 $^1$H NMR Study

The NMe$_3$ adducts prepared in the reaction cell were condensed into an NMR tube at 77 K and d$_8$-toluene was added. The spectra recorded at 222 K are listed in table 4.6. A characteristic terminal Ga-H resonance at $\delta_H$ 5.04 ppm was observed. The region of the (CH$_3$)$_2$CHCH$_2$Ga resonances was particularly informative and is illustrated in figure 4.8. In addition to the doublet at $\delta_H$ 0.45 ppm, arising from TIBGa, there is a second doublet to lower field at $\delta_H$ 0.52 ppm and this is split by a coupling of 1 Hz to the GaH proton. Comparison with the spectra from the TEGa system [1], leaves little doubt that this arises from $^i$Bu$_2$GaH.NMe$_3$. There was no sign of the NMe$_3$ adduct of the dihydride, but there was indirect evidence that this species had disproportionated, resulting in the evolution of H$_2$ in the NMR sample (sharp singlet at $\delta_H$ 4.50 ppm). This observation is similar to that produced by the disproportionation of EtGaH$_2$ in the work on TEGa [1].

4.8 IR LPHP of TTBGa

4.8.1 FTIR Study

TTBGa/SF$_6$ mixtures were pyrolysed at laser powers between 1.20-2.15 watts; comparison with the work of Atiya [12] suggested that the approximate maximum cell temperature was around 500-580 K. Figure 4.9 illustrates the progress of the IR LPHP of a mixture of SF$_6$ (10 torr) and TTBGa (as liquid in the cell). The mixture before pyrolysis is shown in (A), and (B) is after exposure to 1.20 watts of laser power for 60 seconds. The principal changes were the generation of 2-methylpropene (identified in the IR LPHP of TIBGa) and the appearance of a broad asymmetric Ga-H-Ga stretch near 1530 cm$^{-1}$, and two further new peaks at 730 and 653 cm$^{-1}$. The former are due to di-tert-butylgallane, which was isolated by cooling the cell to 77 K and pumping away volatile materials (SF$_6$ and 2-methylpropene). Figure 4.9(C) is that of di-tert-butylgallane and in table 4.3 a full list of the spectra and the assignments are given.
<table>
<thead>
<tr>
<th>CHEMICAL SHIFT/ppm</th>
<th>ASSIGNMENT</th>
<th>COUPLING</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45 (d)</td>
<td>([\text{Ga}^{\text{iBu}_3}\text{NMe}_3])</td>
<td>(J=7.2) Hz</td>
</tr>
<tr>
<td>0.52 (d)</td>
<td>([\text{Ga}^{\text{iBu}_2\text{H}}\text{NMe}_3])</td>
<td>(J=7.0) Hz</td>
</tr>
<tr>
<td>1.33 (d)</td>
<td>([\text{Ga}^{\text{iBu}_3}\text{NMe}_3])</td>
<td>(J=6.5) Hz</td>
</tr>
<tr>
<td>1.40 (d)</td>
<td>([\text{Ga}^{\text{iBu}_2\text{H}}\text{NMe}_3])</td>
<td>(J=6.5) Hz</td>
</tr>
<tr>
<td>2.15 (nonet obscured by CD₃ in toluene)</td>
<td>([\text{Ga}^{\text{iBu}_3}\text{NMe}_3])</td>
<td>(J=6.5) Hz</td>
</tr>
<tr>
<td>5.04 (s,br)</td>
<td>([\text{Ga}^{\text{iBu}_2\text{H}}\text{NMe}_3])</td>
<td>(J(\text{Ga-H})=1) Hz</td>
</tr>
</tbody>
</table>
Figure 4.8: $^1$H NMR spectrum of isobutylgallane trimethylamine adducts at 222 K. Only the region of the $\text{CH}_2\text{CH(CH}_3)_2$ protons is shown. The pair of doublets (marked●) between $\delta^H 0.50$ and 0.55 ppm, partially overlapped by an impurity, are assigned to $^i\text{Bu}_2\text{GaH.NMe}_3$, and the strong doublet at $\delta^H 0.47$ ppm to $^i\text{Bu}_3\text{Ga.NMe}_3$. 
Figure 4.9: FTIR spectra showing the formation of $^1$Bu$_2$GaH from the IR LPDP of $^3$Bu$_3$Ga, before (A) and after (B) exposure to 1.20 W of laser radiation for 60 s. Spectrum (C) is that of the pyrolysis product after removal of volatile components; note particularly the bridging Ga-H vibrations marked •.
The symmetric Ga-H stretch at 653 cm\(^{-1}\) only arises after prolonged pyrolysis at the higher laser power end. By analogy with the known chemistry of the TEGa system [1], and the NMR evidence to be described in the next section, this species may be tentatively ascribed to the dihydride, \(\{^1\text{BuGaH}_2\}_n\), formed as a result of a second \(\beta\)-elimination step. It is also worth noting that, at higher laser powers, a metallic mirror of gallium was deposited on the cell walls, in complete contrast to the TEGa system [1], where the gallium deposited was in the form of a grey powder.

4.9 Adduct Formation with NMe\(_3\)

4.9.1 FTIR Study

As with the two previously described systems, the formation of adducts with NMe\(_3\), has proved invaluable in the elucidation of the species involved. An excess of NMe\(_3\) vapour was added to the products isolated in figure 4.9(C), this resulted in the following changes: the broad Ga-H vibration at 1530 cm\(^{-1}\) is replaced by a much narrower peak at 1750 cm\(^{-1}\) and the two Ga-H stretches at 730 and 653 cm\(^{-1}\) are replaced by a single peak near 780 cm\(^{-1}\), as illustrated in figure 4.10. These shifts are ascribed again to the replacement of the bridging Ga-H-Ga units in the native compound to terminal Ga-H bonds in the NMe\(_3\) adduct, based on the similar behaviour observed in the methyl and ethyl compounds [14].

4.9.2 \(^1\text{H}\) NMR Study

It did not prove possible to obtain a spectrum of the native hydride, either due to its involatility or disproportionation into TTBGa and the unstable gallane in solution, since all attempts resulted in the recovery of TTBGa. However, it did prove possible to obtain a \(^1\text{H}\) NMR spectrum of the NMe\(_3\) adduct at 222 K. This spectrum revealed the presence of two very weak, broad Ga-H resonances at \(\delta_\text{H} 4.85\) and \(\delta_\text{H} 4.67\) ppm (cf. 5.09 and 5.00 ppm for Et\(_2\)GaH.NMe\(_3\) and EtGaH\(_2\).NMe\(_3\) [1]) and two GaC(CH\(_3\))\(_3\) resonances at \(\delta_\text{H} 1.33\) and 1.36 ppm, assigned to \(^1\text{Bu}_3\text{Ga}.\text{NMe}_3\) and...
Figure 4.10: FTIR spectrum of \( ^1\text{Bu}_2\text{GaH.NMe}_3 \). Note the terminal Ga-H vibrations marked ⋄.
\( ^t\text{Bu}_2\text{GaH.NMe}_3 \); the close proximity of these is due to the \( \beta \)-protons being relatively insensitive to substitution on the central Ga atom. The two GaH resonances were ascribed to the dialkylgallane and the monoalkylgallane NMe\(_3\) adducts respectively, with the peak at \( \delta_{\text{H}} 1.36 \) ppm assigned to the unresolved \( ^t\text{Bu} \) resonances of both species.

The \( ^1\text{H} \) NMR spectra recorded at room temperature comprised of a singlet at around 1.25 ppm, which varied according to the amount of NMe\(_3\) present. It must therefore be stressed that in this system only very weakly bound NMe\(_3\) adducts were formed, presumably because of the steric bulk of the tertiary butyl groups.

4.10 Discussion and Conclusion

The observations presented in this chapter, when compared with the results of the TEGa study [1], provide unambiguous evidence that the major Ga-containing products in the gas phase pyrolysis of triisopropylgallane, triisobutylgallane, and tri-tert-butylgallane, are the corresponding dialkylgallanes. These are formed by the following \( \beta \)-hydride elimination reactions:

\[
\begin{align*}
^i\text{Pr}_3\text{Ga} & \rightarrow ^i\text{Pr}_2\text{GaH} + \text{CH}_3\text{CH}=\text{CH}_2 \\
^i\text{Bu}_3\text{Ga} & \rightarrow ^i\text{Bu}_2\text{GaH} + (\text{CH}_3)_2\text{C}=\text{CH}_2 \\
^t\text{Bu}_3\text{Ga} & \rightarrow ^t\text{Bu}_2\text{GaH} + (\text{CH}_3)_2\text{C}=\text{CH}_2
\end{align*}
\]

Figure 4.11 shows the conformational structures illustrating the \( \beta \)-hydride elimination reaction. The evidence presented here for a second \( \beta \)-elimination is less clear cut. In the literature there are few unambiguous reports of free dialkylgallanes, although Markova et al. have synthesized diisobutylgallane by refluxing diisobutyl gallium chloride and lithium hydride in ether [9]. However, the present work provides the first observations of diisopropylgallane and di-tert-butylgallane.

At the laser powers used no evidence of a radical bond homolysis mechanism was discovered in both the TIBGa and TTBGa systems. The only hydrocarbon pyrolysis product observed was 2-methylpropene; no radical recombination products such as
Figure 4.11: Schematic diagram illustrating the $\beta$-elimination mechanism for triisopropylgallane ($R^1 = ^i\text{Pr}$, $R^2 = \text{H,Me}$, $R^3 = \text{H}$), triisobutylgallane ($R^1 = ^i\text{Bu}$, $R^2 = \text{H}$, $R^3 = \text{H,Me,Me}$), and tri-tert-butylgallane ($R^1 = ^t\text{Bu}$, $R^2 = \text{Me}$, $R^3 = \text{H}$).
2,5-dimethylhexane were formed. It was surprising, therefore, that in the TIPGa case, at laser powers above 1.13 watts, the product of the recombination of two isopropyl radicals, 2,3-dimethylbutane was observed, but never in excess of the propene generated. Hence in the TIPGa system, the extent of the competition between the radical bond homolysis and β-hydride elimination pathways is much greater than in the TEGa, TIBGa and TTBGa systems. In the future an attempt to trap the isopropyl radical from the laser pyrolysis of TIPGa using ESR matrix isolation is to be carried out [15]. At this point it is worth comparing the TIPGa results with the work carried out by Razuvaev et al. on the thermal decomposition of triisopropyl and triisobutyl indium [16]. In this study triisopropyl indium was decomposed at 473 K and the gaseous products were analysed by mass spectrometry. The major products were 2,3-dimethylbutane and propane, plus a small amount of propene, formed by a radical bond homolysis mechanism, such as:

\[
\begin{align*}
\text{iPr}_3\text{Ga} & \rightarrow \text{iPr}_2\text{Ga}^- + \text{iPr}^- \\
\text{iPr}^- + \text{iPr}^- & \rightarrow (\text{CH}_3)_2\text{CHCH(CH}_3)_2 \\
2\text{CH}_3\text{CHCH}_3^- & \rightarrow \text{CH}_3\text{CH=CH}_2 + \text{CH}_3\text{CH}_2\text{CH}_3
\end{align*}
\]

Similarly triisobutyl indium was pyrolysed at 403 K, in this system the major products were 2-methylpropene and butane and it was concluded by these workers that the vast majority of the isobutyl radicals disproportionate. The radical recombination reaction versus the disproportionation reaction of radicals has been extensively studied for ethyl radicals [17], but this is not true of isopropyl or isobutyl radicals. The above study by Razuvaev et al. is useful, but it must be remembered that In-C bonds are much weaker than the corresponding gallium ones and, as will be discussed in Chapter 5, indium hydrides are relatively unknown; this makes a radical bond homolysis mechanism most favourable.

Another important point to mention is that all three trialkylgallanes reported in this chapter, undergo β-hydride elimination at much lower temperatures than that of TEGa, despite their low volatility. This suggests that the rate-limiting step in the
pyrolysis is the β-elimination step, however, it must be borne in mind that the rate of evaporation may affect the rate of reaction. Presumably the lower activation energy arises as a consequence of either greater steric strain in the starting materials or a greater release of strain in the transition state.

At this point it is appropriate to mention the pronounced effect that the size of the alkyl substituents on the gallium centre has on the Ga-H-Ga bond angle in the dialkylgallanes. The most extreme case of this is found in di-tert-butylgallane, where the immense steric bulkiness of the tertiary butyl groups reduces the asymmetric Ga-H-Ga bridging bond stretch to 1530 cm\(^{-1}\). The dialkylgallanes may be placed in order of decreasing strain as follows:

\[ \text{t}^3\text{Bu}_2\text{GaH}, 1530 \text{ cm}^{-1} > \text{iPr}_2\text{GaH}, 1618 \text{ cm}^{-1} > \text{Et}_2\text{GaH}, 1640 \text{ cm}^{-1} > \text{iBu}_2\text{GaH}, 1658 \text{ cm}^{-1} > \text{Me}_2\text{GaH}, 1705 \text{ cm}^{-1} \] [13].

For the NMe\(_3\) adducts no definite trends can be deduced, as these contain no bridging Ga-H bonds, only terminal bonds, and the apparent (Ga-H\(^t\))\(t\) stretching frequency varies slightly according to the amount of NMe\(_3\) present.

Finally, recent interest in the higher trialkylgallanes has arisen because of their possible potential as precursors for the growth of GaAs and AlGaAs layers [2,3]. Foord and co-workers have investigated the decomposition of TIPGa on a (100) GaAs surface, using modulated beam mass spectrometry and temperature programmed desorption [2]. When compared to TEGa, TIPGa showed lowered carbon incorporation levels. These workers have also carried out a similar investigation using TIBGa and TTBGa [3]. For TIBGa, the surface spectroscopic techniques indicated that adsorbed isobutyl radicals decompose to produce gaseous butene and H\(_2\) at significantly lower temperatures than in the corresponding case for ethyl radicals on GaAs, and this resulted in lowered growth temperatures and reduced carbon incorporation, in comparison with the results obtained for TEGa. However, at higher growth temperatures β-methyl elimination may occur, as previously described for TIBAl by Bent [7], thus causing carbon incorporation. Note no β-methyl elimination
leading to the formation of propene was observed in the IR LPHP of TIBGa. It was initially thought that TTBGa would have the advantage over TIBGa, as it undergoes β-hydride elimination to produce 2-methylpropene just as readily and does not contain any β-methyl groups. But growth rates using TTBGa were extremely slow; this can be explained on consideration of the relative stabilities of the amine adducts. Assuming that butylgallanes are bound to the growth surface in a similar manner as they are in the Lewis acid-base adducts, it is readily apparent that the tert-butyl compound will be attached with much greater difficulty than the less sterically hindered TIBGa. In terms of both low carbon incorporation and an efficient growth rate, it is difficult to single out one of the trialkylgallanes as being superior to the others as a gallium precursor. But in general lower growth rates are inevitable using the less volatile higher trialkylgallanes.
REFERENCES

Chapter Five

IR LPHP of Triethylborane
and Triethyl Indium
5.1 Introduction

The IR LPHP of triethylborane, TEB, triethylalane, TEAL, and triethyl indium, TEIn, were investigated firstly to compare with the highly successful study of TEGa by Grady [1] and most importantly to obtain a complete picture for the mechanism of decomposition of the Group III triethyl compounds. The pyrolysis mechanisms of the trimethyl compounds of Group III have been studied using the technique of IR LPHP. Trimethylalane, TMAl, was investigated by Atiya [2]; in this system the SF$_6$ interacted with the Me$_2$Al radicals, to form dimethylaluminium fluoride. Trimethylgallane, TMGa, and trimethyl indium, TMIn, were pyrolysed by Grady et al. [3] and the present author [4]. In these two systems no interaction with the SF$_6$ took place; only a radical bond homolysis reaction occurred, as Ga-F and In-F bonds are weaker than the corresponding Al-F [5].

The pyrolysis mechanism for TEB has not been extensively studied; this is probably due to it having no direct application in the growth of semiconductor devices. However, the most commonly used boron compound in this industry is trimethylborane, which acts as a precursor for p-type dopants [6]. The most important use of trialkylboranes is in organic synthesis, the most common example being in the hydroboration of alkenes [7].

The thermal decomposition of the higher trialkyls of aluminium has been investigated by a number of workers, and the general consensus of opinion is that β-hydride elimination is the predominant reaction pathway [8-11]. The growth of semiconductor materials, such as AlGaAs, using TEAl has often resulted in low growth rates and poor layer uniformity [12]. This is due to the extremely low vapour pressure of TEAl (ca. 0.04 torr at 298 K), which means that the reactor lines and source have to be heated; a direct consequence of this is premature aluminium deposition. The IR LPHP of TEAl was fraught with difficulties because of the severe involatility and low thermal stability of this compound. Using the techniques available it was not possible to isolate a pure sample of TEAl, free from diethylalane. This problem was also
highlighted by Ziegler et al. for triisobutylalane where $\beta$-elimination is also extremely facile [8]. Therefore the results obtained from the IR LPHP of TEAl are not presented in this thesis [13]. However, as far as can be discerned TEAl also undergoes $\beta$-elimination under the IR LPHP conditions.

There have been relatively few reports of pyrolysis studies being carried out on TEIn in the literature, of which the most notable ones are to be reviewed in the following section. In the present work it was initially hoped that, using the IR LPHP technique, it might have been possible to observe an organoindium hydride. However, hydrides of indium are comparatively unknown in the literature, apart from anionic indium hydride salts of formula $\text{MIn}_3\text{H}$, where $\text{M}=$Li,Na,K and $\text{R}=\text{Me}$ or Et. Compounds of this type were first prepared by Gavrilenko and co-workers in 1979 [14]; unfortunately these particular species are thermally unstable and conclusive evidence for their existence was not achieved. Recently, however, Beachley et al. successfully synthesized the compounds $\text{K[HIn(CH}_2\text{CMe}_3\text{)_3]}$ and $\text{K[HIn(CH}_2\text{CMe}_3\text{)_3]}$, by reacting $\text{In(CH}_2\text{CMe}_3\text{)_3}$ with potassium hydride in pentane at room temperature [15]. Both compounds are stable crystalline solids, which were fully characterized by elemental analysis, molecular weight studies, X-ray diffraction and IR and $^1\text{H}$ NMR spectroscopies.

As part of our recent studies on gas phase exchange reactions, the following two systems were studied using FTIR spectroscopy:

i) trimethyamine alane (TMAA) and trimethyl indium (TMIn);

ii) dimethylalane (DMAIH) and triethyl indium (TEIn) [16,17].

Similar results were obtained for both mixtures, in that immediately on adding the trialkyl indium compound to the reaction cell, highly specular metallic indium was deposited. This is presumably due to exchange reactions taking place, followed by the instantaneous decomposition of the unstable indium hydrides. Interestingly, this may well be the first example of a room temperature deposition of a metal from the gas phase in this kind of system.
The most important application of trialkyl indium compounds is as indium precursors for the manufacture of indium phosphide, InP, and gallium indium arsenide, GaInAs. However, there are a number of problems associated with the MOVPE growth of compound semiconductors using these compounds. In the case of trimethyl indium, TMIn, the main problem is that it is a solid at room temperature. Although high quality films can be grown by heating up the TMIn bubbler and the reactor lines, the sublimination from a solid can cause problems if the surface area of the TMIn crystals in the cylinder changes with time, due to recrystallization by vapour transport. The result of this is an effective vapour pressure that decreases with time during both storage and use [6]. For triethyl indium, TEIn, there exist the problems of both low volatility and thermal stability, coupled with gas phase parasitic reactions with \( \text{AsH}_3 \) and \( \text{PH}_3 \) taking place to produce involatile polymeric materials [18,19]:

\[
\text{Et}_3\text{In} + \text{PH}_3 \rightarrow \text{Et}_3\text{In}:\text{PH}_3 \quad [5.1]
\]

\[
n\text{Et}_3\text{In}:\text{PH}_3 \rightarrow 2n\text{C}_2\text{H}_6 + (\text{EtInPH})_n \quad [5.2]
\]

The consequences of this reaction is that only low growth rates and poor quality materials can be achieved. This premature reaction has also been shown to be significant in the case of TMIn by a number of workers [20,21]. Recent interest has centred around the use of mixed alkyl group indium precursors such as \( \text{Et}_2\text{MeIn} \), as described in Chapter 3, and methyl cyclopentadienyl indium [22]. Adducts of TMIn and TEIn have also been investigated as potential precursors [19,23,24].

In general, however, high quality layers can be grown using TMIn or TEIn by careful adaptation of reactor design [6,25] and conditions; for example, the best results in the TEIn + \( \text{PH}_3 \) system were obtained using a low pressure MOVPE reactor [26].

This chapter begins by reviewing previous pyrolysis studies of both TEB and TEIn, followed by the presentation of the results obtained using the IR LPHP technique and then lastly the final discussion and conclusions.
5.2 Review

5.2.1 Triethylborane

Abuin et al. [27] have studied the gas phase decomposition of TEB in the temperature range 382-487 K, using gas chromatography. For this reaction the activation energy was found to be in the order of 141(5) kJ mol\(^{-1}\). From their results they proposed the following reaction mechanism:

\[ \text{Et}_3\text{B} \rightarrow \text{Et}_2\text{BH} + \text{C}_2\text{H}_4 \]  \[5.3\]
\[ \text{Et}_2\text{BH} + \text{C}_2\text{H}_4 \rightarrow \text{Et}_3\text{B} \]  \[5.4\]
\[ 2\text{Et}_2\text{BH} \rightarrow \text{Et}_2\text{B} (\mu\text{H})_2 \text{BEt}_2 \]  \[5.5\]
\[ \text{Et}_4\text{B}_2\text{H}_2 \rightarrow 2\text{Et}_2\text{BH} \]  \[5.6\]
\[ \text{Et}_2\text{BH} + \text{Et}_3\text{B} \rightarrow \text{H}_2 + \text{products} \]  \[5.7\]

In this system, the re-insertion of ethene into the B-H bond [5.4], is thought to be very favourable, therefore Abuin and co-workers used cyclohexene or ethyne as scavengers of the diethyl borane hydride. This reaction produced:

\[ \text{C}_6\text{H}_{10} + \text{Et}_2\text{BH} \rightarrow \text{Et}_2\text{BC}_6\text{H}_{11} \]  \[5.8\]

with the result that reaction [5.8], became faster than reaction [5.4], thus allowing the amount of ethene to be measured and the extent of reaction [5.3]. The only pyrolysis products reported in this study were ethene and \(\text{H}_2\). It is therefore worth commenting that the detection of, for example, ethane would be limited by the type of column used in the G.C. Although these workers claim that surface effects were negligible, it is difficult to eliminate heterogeneous contributions in conventional pyrolysis techniques.

Barriola and co-workers have devised a novel method for synthesizing TEB, by irradiating gas phase mixtures of diborane and ethene with a cw CO\(_2\) laser [28]. The laser frequency was tuned to coincide with the bands of the fundamental frequencies, \(v_{14}\) of \(\text{B}_2\text{H}_6\) and the \(v_7\) of \(\text{C}_2\text{H}_4\). A thermal explosion was initiated, producing yields of TEB up to 91\%, in the first second of irradiation. The reaction progress was monitored using IR spectroscopy. The final yield of TEB is dependent on the ratio of diborane to ethene; using a ratio of 1:12 a 91\% yield is obtained. Two competing
reactions in this system have been proposed:

$$\text{B}_2\text{H}_6 + 6\text{C}_2\text{H}_4 \rightarrow 2\text{Et}_3\text{B}$$  \[5.9\]

$$\frac{n}{2}\text{B}_2\text{H}_6 \rightarrow (\text{BH})_n + n\text{H}_2$$  \[5.10\]

Therefore the precise mechanism of decomposition for TEB has to date not been fully characterized.

Similarly the mode of decomposition of various other trialkylboranes has not been extensively investigated. However, Buchanan and Creutzberg, in 1962, studied the pyrolysis of trimethylborane in a static system over the temperature range 741-786 K [29]. The reaction was found to be first order, with an activation energy of 234 kJ mol\(^{-1}\). Methane and hydrogen were detected by taking pressure measurements and recording IR spectra. These workers proposed the following reaction mechanism, based on their results:

$$\text{Me}_3\text{B} \rightarrow \text{Me}_2\text{B} \cdot + \text{Me} \cdot$$  \[5.11\]

$$\text{Me} \cdot + \text{Me}_3\text{B} \rightarrow \cdot\text{CH}_2\text{BMe}_2 + \text{CH}_4$$  \[5.12\]

$$\cdot\text{CH}_2\text{BMe}_2 \rightarrow \text{CH}_2 = \text{BMe} \text{ etc.}$$  \[5.13\]

followed by polymerisation steps which would eventually yield hydrogen and the deposition of \((\text{BCH})_n\) on the surface.

Rossi et al. have investigated the pyrolysis of the higher trialkylboranes [30]. They found that triisopropyl and tri-tert-butyl boranes (TIPB and TTBB) undergo thermal isomerization via a four membered transition state to yield the corresponding straight chain isomers at temperatures between 393-423 K. The following activation energies were measured for these processes: TIPB, 121 kJ mol\(^{-1}\) and TTBB, 163 kJ mol\(^{-1}\).

5.2.2 Triethyl Indium

The major investigation of the mechanism of the thermal decomposition of triethyl indium has been carried out by Razuvaev and co-workers [31]. In their experiments TEIn was pyrolysed at 473 K. The volatile hydrocarbon products were analysed by mass spectrometry, while any undecomposed TEIn was hydrolysed and
the extent of the reaction was assessed by the amount of indium metal obtained. The major pyrolysis product in all their experiments was ethane, with small amounts of ethene, butane and butene. Significantly, no $H_2$ was present in any of the hydrolysis gases. Hence they proposed that TEIn undergoes a radical bond homolysis mechanism when it is pyrolysed:

$$\text{Et}_3\text{In} \rightarrow \text{Et}_2\text{In}^\cdot + \text{Et}^\cdot \quad \text{etc.} \quad [5.14]$$
$$\text{Et}^\cdot + \text{Et}_3\text{In} \rightarrow \text{Et}_2\text{InC}_2\text{H}_4^\cdot + \text{C}_2\text{H}_6 \quad [5.15]$$
$$\text{Et}_2\text{InC}_2\text{H}_4^\cdot \rightarrow \text{Et}_2\text{In}^\cdot + \text{C}_2\text{H}_4 \quad \text{etc.} \quad [5.16]$$
$$2\text{Et}^\cdot \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \quad [5.17]$$
$$2\text{Et}^\cdot \rightarrow \text{C}_4\text{H}_{10} \quad [5.18]$$

The ethyl radicals formed undergo disproportionation, recombination and react with the parent compound. It is worth mentioning that the large amount of ethane generated in this system could be partly due to the hydrolysis of TEIn prior to pyrolysis. Razuvaev et al. also studied the photolysis of TEIn. Under these conditions the major decomposition product was butane; therefore the recombination of the ethyl radicals was the more predominant pathway in this case.

Travkin et al. have also investigated the thermal decomposition of TEIn using differential thermal analysis (DTA) [32]. The pyrolysis products were analysed by gas chromatography, and at 773 K the major product was butane, while at 523 K ethane and ethene were the main products formed. A free radical mechanism was proposed, similar to that in the scheme above.

Razuvaev et al. concluded that the mechanism of pyrolysis for TEIn correlates closely with that of TMIn, as studied by Jacko and Price [33]. They studied the pyrolysis of TMIn in a toluene carrier flow system in the temperature range 550-781 K and the activation energy of the reaction was found to be 198 kJ mol$^{-1}$. The following reaction mechanism was proposed:

$$\text{Me}_3\text{In} \rightarrow \text{Me}_2\text{In}^\cdot + \text{Me}^\cdot \quad [5.19]$$
$$\text{Me}_2\text{In}^\cdot \rightarrow \text{MeIn}^\cdot + \text{Me}^\cdot \quad [5.20]$$
MeIn· → In + Me. \[5.21\]

At all temperatures reaction [5.20] follows [5.19] rapidly, while reaction [5.21] occurs at a measurable rate only at temperatures sufficiently high that reactions [5.19] and [5.20] are completed in a very small period of time. Methane is the major product, followed by ethane and ethene, which are formed by the following reactions:

\[
\begin{align*}
2\text{CH}_3\cdot & \rightarrow \text{C}_2\text{H}_6 \quad \text{[5.22]} \\
\text{CH}_3\cdot + \text{C}_2\text{H}_6 & \rightarrow \text{C}_2\text{H}_5\cdot + \text{CH}_4 \quad \text{[5.23]} \\
\text{C}_2\text{H}_5\cdot & \rightarrow \text{C}_2\text{H}_4 + \text{H}^- \quad \text{[5.24]}
\end{align*}
\]

As a preliminary study the IR LPHP of TMIn was carried out [34]. At a cell temperature of approximately 550 K, methane and ethane were formed in the ratio 1:2.4.

### 5.3 Experimental

The purification and handling of the samples used for the IR LPHP of TEB and TEIn have been described in Chapter 2. The purities of both compounds was checked using FTIR and \(^1\)H NMR spectroscopy. The IR spectra of TEB and TEIn are listed in tables 5.1 and 5.2. The apparatus used has been described in Chapter 2.

### 5.4 IR LPHP of TEB

IR LPHP experiments on TEB/SF\(_6\) mixtures were carried out at laser powers ranging from 2.00-7.55 watts. On comparison with the work of Atiya [2], these powers correspond to an approximate maximum cell temperature of between 550-700 K. The extent of the decomposition of TEB was monitored using the asymmetric B-C stretching vibration at 1119 cm\(^{-1}\). Figure 5.1 shows the FTIR spectrum of a mixture of TEB (5 torr) and SF\(_6\) (10 torr), both before (A) and after (B) exposure to 4 watts of CO\(_2\) laser radiation for a period of 14 minutes. The major observable reaction product was ethene (sharp peaks at 949, 1430, 1889, and 2990 cm\(^{-1}\)), accompanied by the deposition of a white/grey solid film on the cell.
<table>
<thead>
<tr>
<th>FTIR</th>
<th>REF. [36]</th>
<th>ASSIGNMENT#</th>
</tr>
</thead>
<tbody>
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<td>2968 (vs)</td>
<td>2967 (vs)</td>
<td>$\nu (C-H)$</td>
</tr>
<tr>
<td>2929 (s)</td>
<td>2933 (vw)</td>
<td></td>
</tr>
<tr>
<td>2890 (s)</td>
<td>2890 (s)</td>
<td></td>
</tr>
<tr>
<td>1472 (m)</td>
<td>1471 (s)</td>
<td>$\delta_{as} (CH_2)$</td>
</tr>
<tr>
<td>1446 (w,sh)</td>
<td>1449 (w,sh)</td>
<td>$\delta_{as} (CH_3)$</td>
</tr>
<tr>
<td>1391 (w)</td>
<td>1391 (mw)</td>
<td>$\delta_s (CH_3)$</td>
</tr>
<tr>
<td>1325 (s)</td>
<td>1325 (s)</td>
<td>Overtone*</td>
</tr>
<tr>
<td>1290 (w,sh)</td>
<td>1290 (w,sh)</td>
<td>$\omega (CH_2)$</td>
</tr>
<tr>
<td>1136 (vw,sh)</td>
<td>1136 (vw,sh)</td>
<td>$\nu_{as} (B-C)$</td>
</tr>
<tr>
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<td>1120 (s)</td>
<td>$\nu_{as} (B-C)$</td>
</tr>
<tr>
<td>1021 (w)</td>
<td>1022 (m)</td>
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</tr>
<tr>
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<td>975 (w,br)</td>
<td>$\rho (CH_3)$</td>
</tr>
<tr>
<td>920 (m)</td>
<td>919 (s)</td>
<td>$\nu (C-C)$</td>
</tr>
<tr>
<td>779 (w)</td>
<td>779 (m)</td>
<td>$\rho (CH_2)$</td>
</tr>
</tbody>
</table>

# Assignments are those of reference [35].
* Overtone/combination band.
### Table 5.2: FTIR Spectrum of Triethyl Indium (cm\(^{-1}\)).

<table>
<thead>
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<th>Assignment#</th>
</tr>
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</tr>
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<td></td>
</tr>
<tr>
<td>2896 (s)</td>
<td></td>
</tr>
<tr>
<td>2862 (s)</td>
<td></td>
</tr>
<tr>
<td>2807 (m,sh)</td>
<td>Overtones</td>
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<tr>
<td>2727 (vw)</td>
<td>Overtones</td>
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<tr>
<td>1462 (m)</td>
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</tr>
<tr>
<td>1413 (w)</td>
<td>(\delta_s) (CH(_2))</td>
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<tr>
<td>1373 (m)</td>
<td>(\delta_s) (CH(_3))</td>
</tr>
<tr>
<td>1226 (w)</td>
<td>-</td>
</tr>
<tr>
<td>1163 (w)</td>
<td>(\omega) (CH(_2))</td>
</tr>
<tr>
<td>1000 (m)</td>
<td>(\rho) (CH(_3))</td>
</tr>
<tr>
<td>953 (m)</td>
<td>(\nu) (C-C)</td>
</tr>
<tr>
<td>926 (m)</td>
<td>(\nu) (C-C)</td>
</tr>
<tr>
<td>622 (m)</td>
<td>(\rho) (CH(_2))</td>
</tr>
</tbody>
</table>

# IR spectrum of TEIn not previously reported, assignments based on IR spectra of TEGa [1], TEB [35] and TEAL [36].
Figure 5.1: FTIR spectra of a mixture of SF$_6$ (10 torr) and TEB (5 torr), before (A) and after (B) exposure to 4 W of laser power for 14 minutes. Features identified arise from SF$_6$ (●), TEB (○), and C$_2$H$_4$ (★).
walls, assumed to be largely boron.

In an attempt to elucidate the reaction mechanism further, NMR samples of the volatile pyrolysis products were collected from experiments using 3.00 and 7.55 watts of laser power respectively. The recorded $^1$H NMR spectra revealed that the pyrolysis products from the IR LPHP of TEB are ethane, ethene, and ethyne; a trace of $H_2$ was also evident from decomposition in the NMR tube. Analysis of the products showed that at low laser power, ethane is the major product, while at the high laser power end, ethene predominates.

5.5 IR LPHP of TEIn

The vapour pressure of TEIn is extremely low (ca 0.20 torr at laboratory temperature) therefore the reaction cell illustrated in figure 2.2 was used in this study. IR LPHP experiments on TEIn and SF$_6$ mixtures were carried out using laser powers of between 1.88-3.00 watts. The maximum cell temperatures attained are likely to be in the range 550-620 K, according to Atiya [2]. Figure 5.2 illustrates the progress of the IR LPHP of a mixture of TEIn (liquid film) and SF$_6$ (10 torr). Spectrum (A) is before pyrolysis and (B) is after exposure to 3.00 watts of CO$_2$ laser radiation for a period of 13 minutes. From the recorded spectra ethene was the only pyrolysis product, coupled with the appearance of a white solid on the walls and windows of the cell, presumably due to indium. Pyrolysis experiments carried out at lower laser powers resulted in the same products, but over a longer time scale.

When the amount of ethene production had reached a maximum, all the volatile components of the cell were condensed into an NMR tube at 77 K. Out-gassed $d_8$-toluene was the solvent used and $^1$H NMR spectra were recorded at 298 K. The major pyrolysis products were butane, ethene, and ethane, in the ratios of 10:1.2:1. This product ratio is in exact accordance with previous studies concerning the ratio of the recombination reaction to the disproportionation reaction for ethyl radicals [37].
Figure 5.2: FTIR spectra of a mixture of SF₆ (10 torr) and TEIn (liquid film), before (A) and after (B) exposure to 3 W of laser power for 13 minutes. Features identified arise from SF₆ (○), TEIn (●), O, and C₂H₄ (⋆).
5.6 Discussion and Conclusion for TEB

Under the conditions of IR LPHP the precise mechanism of the decomposition of TEB is rather inconclusive. However, it must be remembered that boron chemistry is very complex, in terms of both the bridging and polymerisation tendency of boranes [38]. At low laser powers the ratio of ethane to ethene is 1.8:1, plus a trace of \( \text{H}_2 \). This hydrocarbon product ratio is indicative of a radical bond homolysis mechanism:

\[
\text{Et}_3\text{B} \rightarrow \text{Et}_2\text{B}^* + \text{Et}^* \quad \text{etc.} \\
\text{C}_2\text{H}_5^* \rightarrow \text{C}_2\text{H}_4 + \text{H}^* \\
2\text{C}_2\text{H}_5^* \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4
\]

However, the most significant point is that no butane was formed, (from the recombination reaction of ethyl radicals). The presence of \( \text{H}_2 \), formed by a reaction in the NMR tube, could possibly be attributed to the disproportionation of a dialkylborane in solution, but from the work of Buchanan on trimethylborane [29], it was shown that a significant amount of \( \text{H}_2 \) can be formed when a \( \beta \)-elimination route is unavailable and this would not be detected using our techniques.

Conversely at high laser powers the ratio of ethene to ethane was 11.7:1; this suggested a \( \beta \)-elimination mechanism. One possible explanation is that if any gaseous diethylborane was formed it would be instantaneously pyrolysed further, resulting in the subsequent deposition of boron in the reaction cell. Alternatively more complex boron hydrides may be solids and would therefore be undetected. Another interesting observation is that the photosensitiser, \( \text{SF}_6 \), did not participate in the pyrolysis reaction, despite the fact that boron and fluorine form very strong bonds. This might indicate that no diethylborane radicals were generated in the system.

In the future the IR LPHP of trimethylborane needs to be studied, firstly to see if any dimethyl boron fluoride can be isolated, as in the case of \( \text{Me}_2\text{AlF} \) from the IR LPHP of \( \text{TMAl} \) by Atiya [2], and secondly to shed further light on the mode of decomposition of trialkylboron compounds. Also in the near future ESR matrix isolation studies are to be carried out on the TEB system [39].
5.7 Discussion and Conclusion for TEIn

It is readily apparent that under the conditions of IR LPHP, TEIn decomposes exclusively via a radical bond homolysis mechanism and this is the only system studied so far in which a significant amount of butane has been generated. These results are entirely in accord with previous reports on the mode of decomposition for trialkyl indium compounds [31,32]. At the present time the ethyl radicals from both the conventional hot-tube pyrolysis and the IR LPHP of TEIn, are being trapped and studied by the technique of ESR matrix isolation [39]. The products of the IR LPHP of TEIn differ significantly from those of the TEGa system, where the β-hydride elimination mechanism predominates. This is due to the fact that the In-C bond is weaker than the corresponding Ga-C bond, coupled with the instability of compounds containing In-H bonds, as was clearly demonstrated in the exchange reaction between TEIn and DMAIH, presented in section 5.1. The use of TEIn as a growth precursor therefore presents no advantage over the use of TMIn because the decomposition of both species is dominated by radical processes, in complete contrast with the gallium systems described in Chapter 3.
REFERENCES


[34] R. E. Linney, unpublished results.


Chapter Six

IR LPHP of Dimethyl Zinc and Diethyl Zinc
6.1 Introduction

Group II-VI compound semiconductors, such as ZnSe, ZnS, and CdTe, have a large number of applications in visible optoelectronic devices ranging from solar cells and detectors to light emitting diodes, lasers and laser window materials. Traditionally, thin film single crystal layers of these compounds were grown by elemental vapour transport, at temperatures ranging from 873-1173 K \([1,2]\); this technique resulted in poor quality materials. Since the first growth of ZnSe using diethyl zinc, DEZn, and H\(_2\)Se by Manasevit \([3]\), MOVPE has been the most widely used method of growing II-VI semiconductors. However, the most commonly used precursors dimethyl zinc, DMZn, or DEZn, with H\(_2\)Se or H\(_2\)S, can often result in II-VI layers of low uniformity, coupled with poor optical and electrical properties. This is attributed to a premature gas phase reaction occurring between the electron accepting Lewis acids, DMZn or DEZn, and the electron donating Lewis bases, H\(_2\)Se or H\(_2\)S, resulting in the deposition of ZnSe upstream from the substrate \([4-8]\). The precise mechanism by which this reaction occurs is as yet unknown. Two possible reaction mechanisms have been proposed; these include either the initial formation of a weak Zn-Se adduct-like bond, resulting in the formation of ZnSe and methane, or a chain reaction involving radicals:

\[
\text{Me}_2\text{Zn} + \text{H}_2\text{Se} \rightarrow \text{MeZn}^\cdot + \text{HSe}^\cdot + \text{CH}_4 \quad [6.1]
\]

\[
\text{MeZn}^\cdot + \text{HSe}^\cdot \rightarrow \text{ZnSe} + \text{CH}_4 \quad [6.2]
\]

One potential solution to this problem is the use of Group II adduct compounds, for example \(\text{Me}_2\text{Zn}(1,4\text{-dioxan})\) and \(\text{Me}_2\text{Zn(NEt}_3)_2\) \([9-12]\). Despite the fact that ZnSe layers grown from these adduct sources have slightly inferior electrical properties, there are a number of significant advantages associated with their use. Foremost is the inhibition of the pre-reaction with H\(_2\)Se; the precise mechanism of this remains unproven, but there is evidence to suggest that the N or O donor ligands trap the radical intermediates which lead to premature ZnSe deposition. Other benefits are that the adducts can be more easily purified, more convenient carrier gas flow rates and
source temperatures can be used, and high quality ZnSe can be grown at temperatures as low as 473 K.

A similar radical adduct mechanism has been proposed in Group III systems [13]. Therefore as a preliminary project the IR LPHP of TMAI + NMe₃ mixtures was investigated [14]. It was concluded from the results obtained that the NMe₃ trapped the Me₂Al radicals formed during the pyrolysis, preventing them reacting with the photosensitiser, SF₆, to form dimethyl aluminium fluoride; this mechanism was clearly demonstrated by the work of Atiya on the IR LPHP of TMAI [15]. In an attempt to elucidate this mechanism further, ESR matrix isolation work is to be carried out on this system. Currently the IR LPHP of DMZn and amine mixtures is also being studied, in order to study the effect of adduct formation [16].

In this chapter, the IR LPHP of both DMZn and DEZn have been investigated and the first reported evidence of DEZn undergoing a β-hydride elimination is presented. This chapter begins by reviewing the previous works on DMZn and DEZn, there then follows the presentation of the results, discussion and the final conclusions. The work contained in this chapter is to be found in J. Mater. Chem., 1993, 3, 587.

6.2 Review

6.2.1 Dimethyl Zinc

The most extensive study of the thermal decomposition of DMZn was carried out by Dunlop and Price in 1970 [17]; this was a re-investigation of earlier work [18,19]. DMZn was pyrolysed in a toluene carrier system, at temperatures between 823-1015 K. The gaseous products were analysed by gas chromatography. A two step mechanism was proposed:

\[ \text{Me}_2\text{Zn} \rightarrow \text{MeZn}^* + \text{Me}^* \quad [6.3] \]
\[ \text{MeZn}^* \rightarrow \text{Zn} + \text{Me}^* \quad [6.4] \]

in which the activation energy for reaction [6.3] was found to be 226(8) kJ mol⁻¹. The major pyrolysis product was methane, plus traces of ethane and ethene.
Sokolovskii et al. [20] reported the pyrolysis of DMZn in a sealed ampoule, in the temperature range 555-611 K. GC-MS was employed to monitor the progress of the reaction. Methane was the main product observed; smaller and approximately equal amounts of ethane and propane were also formed. These workers concluded from their results that the pyrolysis temperature had little effect, if any, on the proportions of the reaction products. The reaction scheme proposed involves reactions [6.3] and [6.4] above, followed by radical recombination and abstraction reactions to yield the observed products. Also in complete contrast with the studies of Dunlop and Price [17], it was concluded that the reaction was not first order.

Davies et al. studied the decomposition of DMZn in an MOCVD growth reactor at atmospheric pressure, using \( \text{H}_2 \) as the carrier gas [21]. The progress of the reaction was monitored by removing samples from both in the reactor and the exhaust using mass spectrometry and gas-solid chromatography. The pyrolysis of DMZn in a clean reactor took place in the temperature range 483-723 K; the major hydrocarbon product was methane and the activation energy was found to be in the region of 100 kJ mol\(^{-1}\). Surface effects on the decomposition were investigated; using a reactor internally covered with ZnSe deposits, for example, the effect was that the pyrolysis began at the higher temperature of 533 K and the activation energy was significantly reduced to approximately 69 kJ mol\(^{-1}\). Therefore a marked surface controlled catalytic process dominates in this system, as does the presence of ZnO for the decomposition of DEZn, which will be discussed in the next section.

### 6.2.2 Diethyl Zinc

The thermal decomposition of DEZn using a toluene carrier system was also studied by Price and co-workers [22]. The mechanism of the pyrolysis was investigated over the temperature range 669-762 K and the activation energy was found to be 205(8) kJ mol\(^{-1}\). A two step radical bond homolysis mechanism was proposed:

\[
\text{Et}_2\text{Zn} \rightarrow \text{EtZn}^- + \text{Et}^-
\]  

[6.5]
EtZn\cdot \rightarrow \text{Zn} + \text{Et}\cdot 

[6.6]

in which the second step rapidly follows the first. The overall progress of the reaction was followed by the determination of the residual DEZn by hydrolysis, followed by analysis for zinc by atomic absorption. Both the gaseous products and the hydrolysis gases were analysed using gas chromatography. At 713 K the major product was ethene, together with much smaller quantities of ethane and butane. At 756 K, the amount of ethene further increased, coupled with significant increases in the amount of butane and ethane being produced. The following further radical reactions were proposed for this apparently homogeneous decomposition:

\[ 2\text{C}_2\text{H}_5\cdot \rightarrow \text{C}_4\text{H}_{10} \] [6.7]
\[ 2\text{C}_2\text{H}_5\cdot \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \] [6.8]
\[ \text{C}_2\text{H}_5\cdot \rightarrow \text{C}_2\text{H}_4 + \text{H}\cdot \] [6.9]
\[ \text{H}\cdot + (\text{C}_2\text{H}_5)_2\text{Zn} \rightarrow \text{HZn(C}_2\text{H}_5) + \text{C}_2\text{H}_5\cdot \] [6.10]

Reaction [6.10] is postulated to explain the significant amounts of H$_2$ produced from the hydrolysis of the residual alkyl. In the presence of ZnO, the decomposition of DEZn became a heterogeneous catalysed process, with an activation energy of 100(8) kJ mol$^{-1}$. However, it was concluded from the results obtained that the ethyl radicals formed in this system were unaffected by the coated surface.

Dyagileva et al. reported the gas phase pyrolysis of DEZn in the temperature range 523-568 K [23]. The DEZn was pyrolysed in a clean sealed glass vessel and the decomposition products were analysed by mass spectrometry. At 568 K the major product was ethane, followed by butane and ethene; very small quantities of hydrogen, butene, hexene, hexane, octene and octane were also observed. A radical bond homolysis mechanism was proposed similar to that of the above scheme postulated by Price et al. DEZn was also pyrolysed in the presence of H$_2$, which resulted in an increase in the rate of the decomposition reaction. The H$_2$ was thought to be reacting with the ethyl radicals:

\[ \text{C}_2\text{H}_5\cdot + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}\cdot \] [6.11]
$H^+ + (C_2H_5)_2Zn \rightarrow C_2H_6 + C_2H_5^* + Zn$  \[6.12\]

based on the increase in the yield of ethane.

These workers also proved that the metallic zinc liberated during the pyrolysis of DEZn did not affect the rate of decomposition. However, when the solid pyrolysis products were applied to the inner walls of the vessel and exposed to air prior to pyrolysis, the decomposition of DEZn was partially catalysed. Evidently the water adsorbed by the surface of the solid coating hydrolyses the DEZn, producing a considerable yield of ethane compared to other products. This was regarded as the initiation of a chain reaction by the walls of the vessel, thus facilitating the generation of radicals. These workers also discuss briefly the possible intra- or intermolecular disproportionation of ethyl groups.

It is apparent from the review of the growth of II-VI semiconductors by Mullin et al. [24] that pyrolysis data, be it homogeneous or heterogeneous, for the alkyls is at present very limited and the precise mechanisms involved in the formation of II-VI compounds has not been directly investigated. In the above reviews for DMZn and DEZn, the proposed reaction mechanisms have rested heavily on the distribution of the hydrocarbon end products and the primary intermediates, such as EtZn radicals, have not yet been reported.

### 6.3 Experimental

The purities of DMZn and DEZn were checked using FTIR and $^1H$ NMR spectroscopy. Tables 6.1 and 6.2 list the reported IR spectra of DMZn and DEZn, together with their assignments. The purification and handling of the compounds, together with the apparatus used for the pyrolysis experiments have been described in Chapter 2.
### TABLE 6.1: FTIR SPECTRUM OF DIMETHYL ZINC (cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>FTIR</th>
<th>REF.[25]</th>
<th>ASSIGNMENTS#</th>
</tr>
</thead>
<tbody>
<tr>
<td>3050-2950</td>
<td>-</td>
<td>Rotational fine structure (Q-branches)</td>
</tr>
<tr>
<td>2966 (s)</td>
<td>2966 (s)</td>
<td>(\nu_{as',s}(CH_3))</td>
</tr>
<tr>
<td>2920 (s)</td>
<td>2915 (s)</td>
<td>(\nu_{as,s}(CH_3))</td>
</tr>
<tr>
<td>2849 (m)</td>
<td>2843 (m)</td>
<td>(\delta_{as}(CH_3))</td>
</tr>
<tr>
<td>-</td>
<td>2097 (w)</td>
<td>(\delta_{s}(CH_3))</td>
</tr>
<tr>
<td>-</td>
<td>1892 (w)</td>
<td>(\delta_{s}(CH_3))</td>
</tr>
<tr>
<td>1793 (vw)</td>
<td>1786 (w)</td>
<td>Overtones*</td>
</tr>
<tr>
<td>1705 (vw)</td>
<td>1695 (w)</td>
<td>(\delta_{as}(CH_3))</td>
</tr>
<tr>
<td>-</td>
<td>1617 (w)</td>
<td>(\delta_{as}(CH_3))</td>
</tr>
<tr>
<td>1306 (m)</td>
<td>1301 (m)</td>
<td>(\nu_{as}(Zn-C))</td>
</tr>
<tr>
<td>1295 (w)</td>
<td>-</td>
<td>(\nu_{as}(Zn-C))</td>
</tr>
<tr>
<td>1194 (m)</td>
<td>1183 (m)</td>
<td>(\nu_{as}(Zn-C))</td>
</tr>
<tr>
<td>1174 (m)</td>
<td>-</td>
<td>(\nu_{as}(Zn-C))</td>
</tr>
<tr>
<td>-</td>
<td>1112 (w)</td>
<td>Overtones*</td>
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<tr>
<td>702 (vs)</td>
<td>704 (s)</td>
<td>(\nu(CH_3))</td>
</tr>
<tr>
<td>644 (s)</td>
<td>644 (m)</td>
<td>(\nu(CH_3))</td>
</tr>
<tr>
<td>623 (vs)</td>
<td>613 (vs)</td>
<td>(\nu(CH_3))</td>
</tr>
<tr>
<td>604 (vs)</td>
<td>-</td>
<td>(\nu(CH_3))</td>
</tr>
</tbody>
</table>

# Tentative assignments are those of reference [25].

* Overtones/comparison bands.
### TABLE 6.2: FTIR SPECTRUM OF DIETHYL ZINC (cm⁻¹).

<table>
<thead>
<tr>
<th>FTIR</th>
<th>REF. [26]</th>
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<tr>
<td>2953 (vs)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2915 (vs)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2884 (vs)</td>
<td>-</td>
<td>$\nu_{as'}(C-H)$</td>
</tr>
<tr>
<td>2874 (vs)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2820 (m)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1487 (w,sh)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1469 (m)</td>
<td>1479</td>
<td>$\delta_{as}(CH_3)$</td>
</tr>
<tr>
<td>1461 (sh)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1422 (w)</td>
<td>-</td>
<td>$\delta(CH_2)$</td>
</tr>
<tr>
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<td>1383</td>
<td>$\delta_s(CH_3)$</td>
</tr>
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<td>1375</td>
<td>$\delta_s(CH_3)$</td>
</tr>
<tr>
<td>1236 (w)</td>
<td>1215</td>
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<td>1180</td>
<td>$\rho(CH_3)$</td>
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<tr>
<td>1034 (w)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>993 (s)</td>
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</tr>
<tr>
<td>987 (s)</td>
<td>985</td>
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<tr>
<td>955 (w)</td>
<td>959</td>
<td>$\rho(CH_3) + \nu(C-C)$</td>
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<td>615</td>
<td></td>
</tr>
<tr>
<td>572 (s)</td>
<td>569</td>
<td>$\nu_{as}(C-Zn-C) + \delta(Zn-C-C)$</td>
</tr>
</tbody>
</table>

# Tentative assignments based on reference [26].
6.4 IR LPHP of Dimethyl Zinc

DMZn/SF$_6$ mixtures were pyrolysed at laser powers of between 2.25-7.00 watts. Figure 6.1 illustrates an FTIR spectrum of one particular experiment using 26 torr of DMZn (an excess pressure was required as DMZn is an intrinsically weak IR absorber) and 10 torr of SF$_6$, both before (A) and after (B) exposure to 7.00 watts of laser radiation for a total of 4 minutes. During the pyrolysis the maximum cell temperatures reached are estimated to be in the region of 580-690 K, according to Atiya [15]. The progress of the reaction was monitored by following the decreasing intensity of the $\nu_{\text{as}}$(Zn-C) band at 607 cm$^{-1}$. The only observable pyrolysis product in the FTIR spectra was methane, which was accompanied by a considerable amount of zinc deposition on the cell walls. However, after the pyrolysis was complete the volatile contents of the reaction cell were condensed into an NMR tube at 77 K. The $^1$H NMR study revealed the pyrolysis products to be methane, ethane and ethene in the ratio 4:1:1; plus a trace of ethyne.

6.5 IR LPHP of Diethyl Zinc

IR LPHP experiments on DEZn/SF$_6$ mixtures were carried out at laser powers ranging from 1.33-3.73 watts. Because of the inhomogeneous temperature profile, temperatures can only be estimated based on the work of Atiya [15], which suggests that these powers correspond to maximum cell temperatures in the range 520-630 K. Figure 6.2 shows the FTIR spectrum of a mixture of DEZn (5 torr) and SF$_6$ (10 torr) before (A) and after (B) exposure to 2.50 watts of laser radiation for 200 seconds. The most obvious changes are loss of DEZn features, the production of ethene (sharp structured peaks at 949, 1430, 1889, and 2990 cm$^{-1}$) and a strong broad absorption band centred near 1450 cm$^{-1}$. The hydrocarbon products were further quantified by condensing them into an NMR tube at 77 K, followed by the addition of d$_8$-toluene. The recorded $^1$H NMR spectrum identified the volatile pyrolysis products to be ethene and ethane in a molar ratio of 1.5-2.0:1; significantly no butane was detected.
Figure 6.1: FTIR spectra of a mixture of SF$_6$ (10 torr) and DMZn (26 torr), before (A) and after (B) irradiation at 7 W of laser power for 4 minutes. Features marked are identified as follows: (○) = SF$_6$, (∗) = DMZn, and (●) = CH$_4$. 
Figure 6.2: FTIR spectra showing the formation of ZnH$_2$ from the IR LPHP of DEZn (5 torr) and SF$_6$ (10 torr), before (A) and after (B) exposure to 2.50 W of laser power for 200 s. Features marked are assigned as follows: (O) = SF$_6$, (▲) = ZnH$_2$, and (●) = C$_2$H$_4$. Spectrum (C) is the pyrolysis cell after evacuation of all volatile components.
The 1450 cm\(^{-1}\) band remained after the volatile contents of the cell had been pumped away, as shown in figure 6.2(C). This involatile product was visible as a grey, white, or sometimes colourless, powder on the walls and windows of the cell. Most interestingly of all is that if \(\sim 1\) torr of TMAI or TEGa was previously pyrolysed in the cell at a high laser power, thus producing Al or Ga metal on the front ZnSe window, the intensity of the 1450 cm\(^{-1}\) IR band could be considerably increased. This phenomenon evidently arose from increased deposition onto the cell windows, when the anti-reflective coating of Al\(_2\)O\(_3\) on the ZnSe windows is covered up by a thin film of metal.

The identification of the solid carrier of the 1450 cm\(^{-1}\) IR band, thought to be ZnH\(_2\), was not straightforward. Elemental analysis proved of little value, because of the unavoidable contamination by zinc metal and other unidentified solid products. Meaningful mass spectrometry was difficult because of the involatility of the ZnH\(_2\). Therefore in order to prove that the deposited material was indeed ZnH\(_2\), an authentic sample of ZnH\(_2\) was synthesized from the exchange reaction of DMZn and DMAIH, to be described in the following section.

6.6 Exchange Reaction Between DMAIH and DMZn

6.6.1 FTIR Study

In this experiment in order to obtain an excess of dimethylalane, DMAIH, which has a very modest vapour pressure, (ca 2.00 torr at room temperature) the reaction cell was cooled to 77 K and DMAIH was condensed into the hollow. This temperature was maintained while 25 torr of DMZn was added. The cell was then gradually allowed to warm up to room temperature, whereupon a white crystalline solid layer formed on the front ZnSe window. FTIR spectra were recorded continuously throughout this process and from these it can be deduced that the white solid formed, as the prominent \(\nu(\text{Al-H})\) vibration at 1789 cm\(^{-1}\) in DMAIH, and peaks ascribed to DMZn had decreased significantly in intensity. However, new peaks were formed,
Figure 6.3: FTIR spectra of ZnH$_2$ (A) and ZnD$_2$ (B), produced in the exchange reaction between DMZn and DMAIH or DMAID. Features marked (●) or (○) arise from the Zn-H(D) stretching vibration in ZnH$_2$ or ZnD$_2$ and features marked (*) arise from methyl bound Al groups entrained in the deposited solid.
which closely resembled those assigned to $\text{Me}_2\text{Al(\mu H)(\mu Me)AlMe}_2$ in DMAIH/TMAI mixtures, to be described in Chapter 7.

Figure 6.3(A) illustrates the FTIR spectrum recorded after the volatile by-products had been pumped away. Practically all that remained was a strong broad absorption at $1450 \text{ cm}^{-1}$, analogous with that obtained in the IR LPHP of DEZn. Elemental analysis of this white solid gave the following results: C, 3.45; H, 2.81; Zn, 67.20%. This result is consistent with the additional peaks in figure 6.3 being due to methyl groups bound to aluminium entrained in the white solid.

Further evidence that the broad feature at $1450 \text{ cm}^{-1}$ arises from a Zn-H vibration was confirmed by the analogous exchange reaction between DMZn and DMAI\text{D}. Figure 6.3(B) shows the FTIR spectrum obtained on pumping out the cell. The Zn-H vibration had shifted down to $1090 \text{ cm}^{-1}$, which is approximately the $\sqrt{2}$ expected for the isotope shift.

6.6.2 $^1\text{H NMR Study}$

As additional confirmation of the above results, the vapour pressure of DMAIH was condensed into an NMR tube at 77 K, followed by the addition of a similar pressure of DMZn. This resulted in the immediate formation of the white solid, tentatively ascribed to ZnH$_2$, in the NMR tube. Then out-gassed $d_8$-toluene was distilled into the tube at 77 K. The ZnH$_2$ was found to be completely insoluble in this solvent, and not surprisingly the recorded spectra resembled those of DMAIH/TMAI mixtures in solution. However, most importantly, no features ascribable to zinc species were detected.

6.7 Exchange Reaction Between DMAIH and DEZn

For completeness, the room temperature gas phase reaction between DEZn and DMAIH was investigated. The immediate result of mixing DEZn with DMAIH in the reaction cell was the deposition of a white/grey solid. This product exhibited a number
of disparities in its properties from those of ZnH$_2$ produced in the DMZn + DMAIH system. The most significant ones are that it was non-crystalline, and decomposed to metallic zinc after a period of hours. This reaction was not studied further as the results were somewhat irreproducible.

6.8 Analysis of ZnH$_2$ Samples

Further evidence that the pyrolysis product was definitely ZnH$_2$ was achieved by carrying out the following tests.

6.8.1 Pyrolysis Behaviour

On heating the surface of the cell to approximately 383-393 K by means of resistive heating tape, both the laser pyrolysis product and the authentic ZnH$_2$ decomposed to yield highly specular metallic zinc, together with a gas undetectable by IR (presumably H$_2$); at the same time, the broad 1450 cm$^{-1}$ IR band disappeared. Under conventional hot-walled pyrolysis conditions the cell walls would normally be held at 573-773 K, and thus any ZnH$_2$ produced would be immediately destroyed [22].

6.8.2 Reaction With Air

The products proved to be unreactive with air over a period of a few days, consistent with previous reports in the literature of ZnH$_2$ [27,28]. This also rules out any residual Et-Zn compounds as the IR carrier, since these are readily oxidised or hydrolysed.

6.8.3 Reaction With Pyridine

Each of the ZnH$_2$ products was dissolved in d$_5$-pyridine, in accordance with the previously reported reaction of ZnH$_2$ with pyridine by De Koning et al. [29]. An NMR sample of the deposited ZnH$_2$ from the pyrolysis, was obtained by washing the reaction cell with d$_5$-pyridine, for approximately 20 minutes. The resultant pale yellow solution was then distilled into an NMR tube at 77 K. A few milligrams of the ZnH$_2$ produced from the DMZn + DMAIH exchange reaction was placed directly into an
NMR tube, which was then evacuated, and out-gassed d$_5$-pyridine was added at 77 K. On warming up to room temperature the sample began to effervesce. After several hours the solution became increasingly deeper yellow in colour and after a couple of days, the deposition of metallic zinc at the bottom of the NMR tube was observed. As additional clarification, a small pressure of both DMZn and DMAIH was condensed into an NMR tube, followed by the distillation of d$_5$-pyridine.

$^1$H NMR spectra for all three samples were recorded at room temperature. The spectra all gave rise to similar features; figure 6.4 illustrates the $^1$H NMR spectrum of the ZnH$_2$, from the pyrolysis, in d$_5$-pyridine. In addition to features arising from residual protonated pyridine (δ$_H$ 7.0-9.0 ppm), the spectrum shows a strong broad singlet at δ$_H$ 4.8-5.0 ppm, and a sharp, weaker, singlet at δ$_H$ 3.4 ppm. The downfield resonance proved very temperature and concentration sensitive, strongly suggestive of a reversible association in solution. Over a period of a few weeks, this downfield resonance decayed slightly, while the upfield resonance increased in intensity.

On comparison of the spectra obtained with the results of De Koning et al., the downfield feature was ascribed to Zn-H resonances in the pyridine adducts I and II, and the upfield resonance to the 4-hydrido pyridyl resonances of the adducts II and III. The structures of these pyridine adducts of ZnH$_2$ are illustrated in figure 6.5. De Koning et al. also observed a slow I$\rightarrow$II$\rightarrow$III conversion over a period of a few days, and furthermore isolated from the solution a solid whose empirical formula suggested the formation of Zn-H-Zn bridges [29]. In the present work the results obtained are not in exact agreement with those of De Koning et al., in that the Zn-H bond appears to be more stable, but the results can be compared with previous reports that Zn-H resonances occur between 4.0-5.0 ppm.
Figure 6.4: $^1$H NMR spectrum of ZnH$_2$ from the IR LPHP of DEZn, in d$_5$-pyridine at 298 K.
Features marked (☆) arise from the residual protonated pyridine. (●) singlet at 4.90 ppm is
ascribed to Zn-H resonances in the pyridine adducts I and II and (○) singlet at 3.40 ppm to the
4-hydrido pyridyl resonances of the adducts II and III, shown in figure 6.5.
Figure 6.5: Structures of ZnH₂ pyridine complexes.
6.9 Discussion and Conclusions

The IR and chemical evidence described above demonstrate conclusively that ZnH$_2$ is a major product of the homogeneous pyrolysis of DEZn. The proposed route for the production of ZnH$_2$ is a double $\beta$-hydride elimination:

\[
\begin{align*}
\text{Zn(C}_2\text{H}_5)^- & \rightarrow \text{HZn(C}_2\text{H}_5) + \text{C}_2\text{H}_4 \quad [6.13] \\
\text{HZn(C}_2\text{H}_5) & \rightarrow \text{ZnH}_2 + \text{C}_2\text{H}_4 \quad [6.14] \\
\text{C}_2\text{H}_4 + \text{ZnH}_2 & \rightarrow \text{Zn} + \text{C}_2\text{H}_6 \quad [6.15]
\end{align*}
\]

In contrast with the TEGa system no EtZnH was detected, which was not surprising as organozinc hydrides are known to be stable only in the presence of strong Lewis bases [29,30]. The absence of butane in the hydrocarbon products suggests that a radical bond homolysis mechanism plays only a minor role, since it is the major product in the IR LPHP of TEIn; see Chapter 5. The small amount of ethane observed in the IR LPHP process is thought to arise from two sources, either from the unavoidable traces of hydrolysis of the DEZn during the filling of the cell, or from a surface-catalysed reduction of ethene by the deposited ZnH$_2$, as in reaction [6.15] above.

It is also of interest to note that considerable quantities of H$_2$ were observed in the conventional pyrolysis study by Price et al. [22]. In that work, the formation of H$_2$ was thought to be from the decomposition of the ethyl radical, but our evidence suggests that it arises from the decomposition of the ZnH$_2$ on the hot walls of the reactor. Another important observation from the work of Price et al. is the generation of H$_2$ on hydrolysis of the residual DEZn, which suggests the presence of Zn-H bonds. However, the production of considerable quantities of butane in the conventional pyrolysis study does suggest the formation of ethyl radicals. On the other hand, it is well known that organometallic pyrolyses are extremely sensitive to surface catalysis (especially by oxides), and it is therefore possible that butane arises from a heterogeneous contribution not significant in laser pyrolysis. This fact may also explain the apparent enhancement of deposition of ZnH$_2$ onto windows pre-coated
with Ga or Al; since the ZnSe windows used in the laser pyrolysis are coated with an anti-reflection $\text{Al}_2\text{O}_3$ layer, the window surface may catalyse the decomposition of the $\text{ZnH}_2$. The laser pyrolysis of DMZn results only in metallic zinc, methane, ethane and ethene, no $\text{ZnH}_2$ was formed, thus the mode of decomposition is, as expected, radical bond homolysis.

As the IR LPHP of DEZn results in the formation of $\text{ZnH}_2$, it is appropriate to include here a review of known zinc hydride chemistry. The first report of a hydride of zinc was by Wiberg and co-workers in 1951 [31]. Few experimental details were given in their study, but zinc dihydride was alleged to be the major product in the following two reactions carried out in ether:

$$\text{ZnI}_2 + 2\text{LiAlH}_4 \rightarrow \text{ZnH}_2 + 2\text{AlH}_3 + 2\text{LiI} \quad [6.16]$$

$$3\text{ZnCl}_2 + 2\text{AlH}_3 \rightarrow 3\text{ZnH}_2 + 2\text{AlCl}_3 \quad [6.17]$$

In the same year, Barbaras et al. [27] reported that the most satisfactory method they had developed for the preparation of $\text{ZnH}_2$ was by reacting DMZn with a diethyl ether solution of lithium aluminium hydride, according to the equation:

$$\text{Zn}(\text{CH}_3)_2 + 2\text{LiAlH}_4 \rightarrow \text{ZnH}_2 + 2\text{LiAlH}_3\text{CH}_3 \quad [6.18]$$

$\text{ZnH}_2$ was isolated as a white, non-volatile, solid, which was insoluble in ether, and elemental analysis gave: Zn, 93.6; H, 2.96%. These authors also suggested that $\text{ZnH}_2$ could be synthesized by reacting DMZn and DMAIH.

Bluke and co-workers prepared $\text{ZnH}_2$ by reacting zinc dichloride and lithium aluminium hydride in THF at either 273 K or 303 K [32].

Watkins and Ashby investigated further the reaction between dimethyl zinc and lithium aluminium hydride, in both diethyl ether and THF [33]. They discovered that the reaction products formed were dependent on both the solvent used and the molar ratios of the reactants used. The following reaction schemes were proposed using THF:
IR and $^1$H NMR spectroscopic studies were used to examine the reaction products in solution, and the proposed structures of the trimetal complexes are shown in figure 6.6. These were based on the observation of strong, broad IR absorptions centred at 1400 cm$^{-1}$ and 1660 cm$^{-1}$ for structure (A). These bands were assigned to a double hydrogen bridging stretch and a terminal Al-H stretch. For structure (B), an additional vibration at 1500 cm$^{-1}$ was recorded, and this was ascribed to a Zn-H-Al stretch. The proposed reactions that took place in diethyl ether were:

\[
\begin{align*}
2\text{Zn(CH}_3)_2 + \text{LiAlH}_4 & \leftrightarrow \text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4 \quad [6.19] \\
3\text{Zn(CH}_3)_2 + 2\text{LiAlH}_4 & \leftrightarrow \text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4 + \text{LiZn(CH}_3)_2\text{AlH}_4 \quad [6.20] \\
\text{Zn(CH}_3)_2 + \text{LiAlH}_4 & \leftrightarrow \text{LiZn(CH}_3)_2\text{AlH}_4 \quad [6.21]
\end{align*}
\]

The mechanism of these reactions is thought to be the initial formation of the trimetal complexes (A) and (B) as illustrated in figure 6.6, followed by their subsequent disproportionation into ZnH$_2$ and the corresponding lithium aluminium hydride. This claim is supported by the observation of IR bands consistent with those recorded for the dimethyl zinc and lithium aluminium hydride in THF as described. Watkins and Ashby also prepared ZnH$_2$ by reacting dimethyl zinc and aluminium hydride in diethyl ether or THF at room temperature [28]. A white, air sensitive granular solid was isolated from the solution, which decomposed at 363 K yielding zinc and H$_2$.

Dergachev et al. studied the exchange reaction between aluminium hydride and zinc tetrahydroborate in diethyl ether, using IR spectroscopy and chemical analysis [34]. A white precipitate ascribed to ZnH$_2$ was formed, which decomposed at 353 K yielding H$_2$. The IR spectrum of this product showed broad bands at 500 cm$^{-1}$ and 1500 cm$^{-1}$, which were assigned to a Zn-H deformation and stretch respectively. When stored at room temperature this solid decomposed after 8-12 days to zinc metal.
Proposed structures of the trimetal complexes:

Li₂[Zn(CH₃)₂AlH₄] (A) and Li₂[Zn(CH₃)₄AlH₄] (B) from reference [33].

Figure 6.6
The equation for the reaction is as follows:

\[ \text{Zn(BH}_4\text{)}_2 + 2\text{AlH}_3 \leftrightarrow \text{ZnH}_2 + 2\text{AlH}_2\text{BH}_4 \]  \[ 6.26 \]

De Koning and co-workers prepared zinc hydride by treating diethyl zinc with lithium aluminium hydride in diethyl ether [29]:

\[ \text{Zn(C}_2\text{H}_5\text{)}_4 - 2\text{LiAlH}_4 \rightarrow \text{ZnH}_2 + 2(\text{LiAlH}_3\text{Et}) \]  \[ 6.27 \]

The ZnH\textsubscript{2} formed was isolated by centrifugation and elemental analysis revealed: H, 3.3; Zn, 93.7; Al, 0.5; Li, 1.0%. The physical properties of this product are consistent with the previously described reports. A detailed study of the reaction between ZnH\textsubscript{2} and pyridine was also carried out by these workers; this has already been described in section 6.8.3.

Bell and Coates, in 1968, prepared one of the first organozinc hydride complexes: \[(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N(CH}_3\text{)}\text{ZnH}\], by heating ZnH\textsubscript{2} and trimethyl ethylene diamine in toluene at 323 K [30]. An IR spectrum of this compound exhibited a broad absorption centred at 1825 cm\textsuperscript{-1}, which was ascribed to be a terminal Zn-H stretching vibration. The \textsuperscript{1}H NMR spectrum of this compound in benzene was later recorded by De Koning et al. [29], where the Zn-H resonance was found to be at \( \delta \text{H} = 4.20 \) ppm.

The stable organozinc hydride, PhZn\textsubscript{2}H\textsubscript{3} was synthesized by Ashby and Goel [35]. These workers discovered this novel compound while they were investigating the reaction of diphenyl zinc with lithium aluminium hydride, in order to see if a triple metal complex containing a phenyl group could be prepared. The reaction scheme proposed is:

\[ 4\text{Ph}_2\text{Zn} + \text{LiAlH}_4 \rightarrow 4\text{PhZnH} + \text{LiAlPh}_4 \]  \[ 6.28 \]
\[ 3\text{PhZnH} \rightarrow \text{PhZn}_2\text{H}_3 + \text{Ph}_2\text{Zn} \]  \[ 6.29 \]

The solid PhZnH was isolated from the THF and then characterised by IR spectroscopy, X-ray powder diffraction and differential thermal analysis, and was found to disproportionate as shown in equation [6.29]. The IR spectrum recorded of the nujol mull of PhZn\textsubscript{2}H\textsubscript{3}, contained the following bands: 1650-1550 cm\textsuperscript{-1}, 1366-1300 cm\textsuperscript{-1}, 618 cm\textsuperscript{-1} and 530 cm\textsuperscript{-1}; these were ascribed to terminal and
bridging Zn-H stretching modes and as Zn-H deformation modes respectively. For the
deuterated analogue, PhZnD3, the Zn-H modes shift accordingly to 1180, 990, 420,
and 365 cm\(^{-1}\) respectively. The PhZnH decomposed at 393 K, with the evolution of
hydrogen and benzene. These workers also attempted to isolate methyl zinc hydride' from the corresponding reaction of dimethyl zinc and lithium aluminium hydride in
THF solution in the ratio 4:1. This was unsuccessful as the MeZnH rapidly
disproportionated to MeZnH3, which decomposed to zinc at room temperature.

De Koning et al. reported the synthesis and characterisation of ethyl zinc hydride
and phenyl zinc hydride monopyridine complexes [36]. These compounds were
prepared at room temperature in THF or benzene:

\[
R_2Zn + ZnH_2 + 2py \rightarrow 2RZnH.py
\]  

[6.30]

where R=Et or Ph and py=pyridine. PhZnH.py was isolated from the clear solution
as a white solid, while EtZnH.py was obtained as a viscous yellow oil. \(^1\)H NMR
spectra of these unstable complexes in benzene were recorded, and the Zn-H
resonance was found to be between 4-5 ppm downfield from TMS. IR spectra were
also recorded, but the results were rather inconclusive, as only broad absorptions
similar to those found in the IR spectrum of ZnH2 were observed.

Wittig and Hornberger isolated LiHZn(C\(_6\)H\(_5\))\(_2\) as a monoetherate by heating LiH
and Zn(C\(_6\)H\(_5\))\(_2\) to 363 K and extracting the resultant solid with ether [37]. Similar
anionic organozinc hydride complexes of the type MH(ZnR\(_n\))\(_n\), (where M=Li, Na,
n=1 or 2; R=C\(_6\)H\(_5\) or C\(_6\)F\(_n\), n=1; R=CH\(_3\), n=1 or 2) have also been prepared this
time using 1,2-dimethoxyethane, THF and diethyl ether, by Kubas and Shriver [38].
IR and Raman spectroscopy, coupled with molecular weight analysis and \(^1\)H NMR
data suggested the existence of a mobile equilibrium:

\[
MHZnR_2 + ZnR_2 \leftrightarrow MH[ZnR_2]_2
\]  

[6.31]

\(^1\)H NMR data for the Zn-H resonance varies from \(\delta H\) 3.40-7.00 ppm, depending on
the alkyl zinc/hydride ratio, and is accounted for by a rapid exchange process.
Figure 6.7: Proposed structures for anionic organozinc hydride complexes. Where $M = \text{Li or Na}$, and $R = \text{C}_6\text{H}_5, \text{C}_6\text{F}_5$ or $\text{CH}_3$. taken from reference [38].
IR spectra were also recorded and the Zn-H vibrational modes were as follows: $\nu_{as} \sim 1250-1700 \text{ cm}^{-1}$ and $\delta_{as} \sim 625-788 \text{ cm}^{-1}$ (for the deuterated analogues Zn-D modes were 900-1200 cm$^{-1}$ and 426-552 cm$^{-1}$ respectively). Based on this evidence a number of possible structures were the proposed, these are illustrated in figure 6.7. A similar structure to B was also proposed by Watkins and Ashby to explain the Zn-H stretching frequencies in the compound NaZn(CH$_3$)$_2$H [39].

To conclude; ZnH$_2$ is well characterized in the literature, while the structure of organozinc hydrides have not been fully investigated as yet.
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Chapter Seven

Exchange Reactions
7.1 Introduction

The growth of AlGaAs by MOVPE has traditionally been carried out using TMAI, TMGa and AsH₃ [1]. However, there are several problems associated with the use of methyl-containing aluminium precursors [2]. Firstly is the fact that aluminium forms very strong bonds with oxygen, and water vapour can be adsorbed onto the growing interface and become incorporated into the solid. Recently this problem has largely been overcome by improvements in reactor design. Secondly, but most important, is the problem of carbon contamination; the source of this is almost certainly TMAI because GaAs layers grown using TMGa under identical conditions show considerably less incorporated carbon [1].

One approach to solving the Al precursor problem has been the development of new compounds with appropriate properties. The initial step in this direction was the use of dimethylalane, DMAIH, by Bhat et al. [3]. These workers carried out decomposition studies, and also the growth and characterisation of AlGaAs layers grown using this compound. The preliminary results obtained suggested that there was very little, if any, carbon contamination in the films grown.

Jones et al. have investigated a number of alternative Al precursors including: Me₃Al.NMe₃, (Me₂AlNMe₂)₂ [4], and (tBuAlMe₂)₂ [5]. None of these showed any advantage over TMAI in lowering carbon incorporation, and some of these precursors are even less convenient to use, i.e. in terms of vapour pressure, preparation, and purification. Jones et al. have also re-examined the work of Bhat on DMAIH. These workers found that AlGaAs layers grown from DMAIH or the adduct, DMAIH.NMe₃, contained similar levels of carbon to those obtained with TMAI and the degree of compositional uniformity was low, which was consistent with the large amount of darkening in the reactor upstream from the substrate [6]. This is due to the lower thermal stability of DMAIH relative to TMAI.

The other alternative Al precursor was triethylalane, TEAl, which is thermally less stable than TMAI due to the facile β-hydride elimination of ethyl groups. Hence it
was thought that TEAl might undergo a cleaner, more rapid, pyrolysis than TMAI. Keuch et al. grew AlGaAs using TEAl, TEGa and AsH$_3$ in a low pressure MOVPE reactor which led to non-detectable levels of carbon [7]. However, ethyl based precursors are extremely susceptible to parasitic gas phase reactions and in addition the low vapour pressure of TEAl (0.04 torr at 300 K) requires both the source and reactor lines to be heated, which subsequently leads to its premature decomposition. The growth of AlGaAs using ethyl aluminium adducts, Et$_3$Al.NMe$_3$ and Et$_2$AlH.NMe$_3$, was also examined by Jones et al. [6,8]. It was thought that these precursors would be less susceptible to pre-reaction with AsH$_3$ and more stable than TEAl. Despite this it was found that neither of these precursors had any significant advantages over TMAI.

Another potential Al precursor is trimethylamine alane (TMAA, AlH$_3$.NMe$_3$), which is a reasonably volatile solid. It was found that atmospheric pressure growth using TMAA and TMGa [9], resulted in AlGaAs in which there was no significant reduction in carbon and that carbon incorporation increased with TMGa mole fraction. Poor layer uniformity and deposition on the reactor inlet were also found. However, low pressure growth using these mixtures resulted in excellent layer uniformity, with no evidence of pre-reaction, but there was again no reduction in the amount of carbon incorporated [10]. Under the same growth conditions AlGaAs was grown using TMAA and TEGa. In this system no carbon was detected; despite this, the thickness uniformity was poorer than in the TMGa case, and there was a downstream decrease in the aluminium content of this alloy [11].

It would seem probable that gas phase processes are responsible for this carbon incorporation, a hypothesis which is borne out by the evidence of deposition prior to the susceptor in atmospheric pressure growth [9]. In order to shed further light on this hypothesis, the gas phase exchange reactions in mixtures of both TMAA + TMGa and TMAA + TEGa were investigated by Grady [12]. In the TMAA + TMGa system features ascribed to the following species were observed: free Me$_2$GaH,
Me₂GaH.NMe₃, MeGaH₂.NMe₃, GaH₃NMe₃, Me₃Al.NMe₃, and Me₂AlH.NMe₃. It is therefore evident that the hydrogen preferentially migrates to the more electronegative gallium centre, and the corresponding increase in methyl groups bound to aluminium explains the observation of carbon contamination [9]. The TMAA + TEGa exchange reaction resulted in the formation of Et₂GaH, Et₂GaH.NMe₃, and EtGaH₂.NMe₃, coupled with the presence of the following species of very low volatility: Et₃Al, Et₃Al.NMe₃, and Et₂AlH.NMe₃. From these observations the results of the growth study using TMAA + TEGa [11] can be rationalized in terms of the facile β-hydride elimination of ethyl groups on the aluminium centre.

Exchange processes between alanes, and also between alanes and gallanes have been extensively studied in solution, principally using ¹H NMR spectroscopy; this is to reviewed in the next section. On the other hand, very little is known of such processes in the gas phase. Recently the successful re-analysis of the IR spectrum of DMAIH [13] has enabled the gas phase exchange reaction between DMAIH and TMAI to be examined. The results of this study are presented in this chapter; all isotopic combinations were used to allow for the inevitable overlap of bands. For completeness, NMR studies of toluene solutions of this mixture were carried out.

7.2 Review

As early as 1962 Hoffmann reported the detection of alkyl group exchange reactions in aluminium trialkyls using variable ¹H NMR spectroscopy [14]. Hoffmann extensively studied mixtures of triisobutylalane and trimethylalane in cyclopentane solution. In this system exchange of alkyl groups takes place, producing dimers which are strongly associated by virtue of their methyl groups. Hoffmann concluded from this study that the propensity for bridging is in the order H>Me>ᵢBu. In this report, Hoffmann also listed the ¹H NMR chemical shifts for a number of Me₃Al + Me₂AlX systems, where X=H, Cl, OMe, OEt, and OᵢBu. These systems are complex not only
because of exchange, but also because of the different molecularities involved.

Williams and Brown in 1966 investigated the exchange of methyl groups between the trimethyl derivatives of Group III [15]. They initially studied the exchange of bridging and terminal methyl groups in TMAl in toluene solution, using variable temperature $^1$H NMR spectroscopy. The spectra recorded were similar to those previously reported in cyclopentane solution [16]. At 208 K resonances ascribed to both bridging and terminal methyl groups were clearly identified. Williams and Brown concluded from their results that the rate of exchange is a first order process with respect to the TMAl dimer. They proposed that TMAl is involved in a two step equilibrium of the form:

$$\text{Al}_2(\text{CH}_3)_6 \leftrightarrow 2\text{Al}(\text{CH}_3)_3 \leftrightarrow \text{Al}(\text{CH}_3)_3 + \text{Al}(\text{CH}_3)_3$$

[7.1]

Dimer solvent-caged solvent-separated monomers monomers

Similar results were obtained for both the TMAl + TMGa and TMAl + TMIn systems in toluene. The rate of exchange was found to depend on the ratio of concentrations of the two components. Williams and Brown concluded that the overall rate-determining process in the above two systems is the formation of solvent separated monomeric TMAl, followed by the rapid exchange of methyl groups with the other trimethyl compound:

$$\text{Al}(*\text{CH}_3)_3 + \text{E}(\text{CH}_3)_3 \rightarrow (*\text{CH}_3)_2\text{Al}(\mu*\text{CH}_3)(\mu\text{CH}_3)\text{E}(\text{CH}_3)_2$$

[7.2]

solvent separated monomer(M*) (E)

$$\rightarrow \text{Al}(\text{CH}_3)_3 + \text{E}(*\text{CH}_3)_3$$

(M) (E*)

Jeffrey and Mole re-examined the exchange reaction between TMAl + TMGa in cyclopentane and toluene solutions using $^1$H NMR spectroscopy [17]. Although their kinetic data was very similar to those of Williams and Brown [15], the interpretation of the results was different in several important respects. However, Jeffrey and Mole
were in agreement with one of the most important postulates of Williams and Brown, in that the dissociation of the TMAI dimer determines the rates of both bridge-terminal equilibration and of exchange with TMGa. The significant differences in interpretation are centred around the fact that Williams and Brown proposed that a solvent cage restricted the rate of exchange between TMAI and TMGa (namely that the rate of the bridge-terminal equilibration in cyclopentane and toluene are very similar). The second discrepancy is that Williams and Brown assumed that TMAI and TMGa exchange only takes place after the TMAI monomers have become separated. Jeffrey and Mole, on the other hand, suggested that the TMAI and TMGa exchange reaction occurs before the two TMAI monomers become separated, and also that both the recombination of TMAI monomers and exchange between the TMAI monomer and TMGa are collision-controlled processes. Jeffrey and Mole then went on to provide further evidence for their postulated mechanism:

\[
\text{Al}_2(\text{CH}_3)_6 \leftrightarrow 2\text{Al}(\text{CH}_3)_3 \quad \text{monomer pair} \quad [7.3]
\]

\[
2\text{Al}(\text{CH}_3)_3 + (\text{CH}_3)_3M \rightarrow \text{(exchange)} \quad [7.4]
\]

by investigating the \(^1\text{H}\) NMR kinetics of exchange between DMZn and TMAI in cyclopentane solution, and also by re-examining the TMAI and the TMAI + TMGa systems [18]. Studies of this nature are always hindered by the possible involvement of the solvent, so it is therefore advantageous to first study the reactions in the gas phase.

A number of hetero-bridged organoaluminium species of the general form \(R_2\text{Al}(\mu X)(\mu Y)\text{AlR}_2\) have been identified by a number of workers, in exchange reactions of the type:

\[
\{R_2\text{AlX}\} + \{R_2\text{AlY}\} \rightarrow \{R_2\text{AlX} \cdot R_2\text{AlY}\} \quad [7.5]
\]

where \(R=\text{Me or Et}\), and the braces indicate an unspecified degree of aggregation. Whether the resultant hetero-bridged compound enjoys a stable existence, or is simply a component in an exchange equilibrium, evidently depends on the rates of reaction.
and its reverse. Smith and Wallbridge have identified an ordering of exchange rates for X and Y groups in such compounds as:

\[
\text{Me} > \text{Et} > \text{Cl, Br, I > SMe, OEt > NMe}_2, \text{CN, F} \quad [7.6]
\]

in keeping with the relative strengths of bridging bonds formed by such groups [19]. Subsequently, Fishwick and these workers with the aid of mass spectrometry and \(^1\)H NMR spectroscopy, were able to demonstrate the synthesis and isolation of compounds featuring groups towards the slow exchange end of the range given in [7.6] simply by heating mixtures of the constituents to about 373-473 K; the list of species produced included \(R=\text{Et, X=NMMe}_2, \text{and Y=Cl, Br, I, OEt, and SMe} [20].\)

Jeffrey et al. [21] carried out a similar study of exchange reactions between dimeric organoaluminium compounds. Based on the results obtained, these workers placed the X and Y groups in order of decreasing capacity for bridge formation as follows: \(^i\)PrO > Cl > Br > PhCC > Ph > Me. The groups at the beginning of the series differ from those towards the end in terms of electronegativity, availability of lone pairs of electrons, and bridge geometry which may result in a higher aluminium-aluminium distance.

Eisch and Rhee have studied the stoichiometry of exchange reactions in mixtures of \(^i\)Bu\(_2\)AlH and \(^i\)Bu\(_2\)AlCl [22], and \(^i\)Bu\(_3\)Al and \(^i\)Bu\(_2\)AlH [23], by variable temperature \(^1\)H NMR and IR spectroscopy. In the latter system, two Al-H resonances were observed; a new peak at \(\delta_H 3.90 \text{ ppm} \) they assigned to the mixed bridged compound, this being considerably shifted downfield from that of pure \(^i\)Bu\(_2\)AlH at \(\delta_H 2.92 \text{ ppm} \). These workers proposed a number of dimeric and trimeric heterobridged structures based on their results.

7.3 Experimental

7.3.1 Preparation Of Chemicals

These were largely synthesized by Drs. R. D. Markwell and S. G. Puntambekar.

i) \((\text{CH}_3)_3\text{Al}, \text{trimethylalane, was a gift from Epichem Ltd.}\)
ii) $(\text{CD}_3)_3\text{Al}$, fully deuterated trimethylalane, was prepared from $(\text{CD}_3)_2\text{Hg}$ and Al powder subjected to ultrasound [24].

iii) $(\text{CH}_3)_2\text{AlH}$, dimethylalane, was a gift from Epichem Ltd.

iv) $(\text{CH}_3)_2\text{AID}$, dimethyldeuteroalane, was prepared according to the method of Wartik and Schlesinger [25], i.e. by heating $(\text{CH}_3)_3\text{Al}$ and excess $\text{LiAID}_4$ to 363-368 K in the absence of solvent, followed by removal of the volatile $(\text{CH}_3)_3\text{Al}$ and purification by trap-to-trap distillation.

v) $(\text{CD}_3)_2\text{AlH}$, di(perdeuteromethyl)alane, was similarly prepared using $(\text{CD}_3)_3\text{Al}$ and $\text{LiAID}_4$.

All materials were handled at all times on a rigorously pre-conditioned vacuum line as described in Chapter 2.

7.3.2 Characterization of Chemicals

Isotopic purity of all compounds was checked using $^1\text{H}$ NMR spectroscopy and was estimated to be $>99\%$ for all species.

i) $(\text{CH}_3)_3\text{Al}$, trimethylalane

The FTIR spectrum of $(\text{CH}_3)_3\text{Al}$ vapour is shown in figure 7.1 and the assignment of the spectra is listed in table 7.1. The vibrational spectra of TMAIAl in the vapour phase has been extensively studied [26-28]. At room temperature $(\text{CH}_3)_3\text{Al}$ is largely dimerized through bridging methyl groups, but at elevated temperatures becomes almost entirely monomeric [28-30]. The FTIR spectrum of $(\text{CD}_3)_3\text{Al}$ vapour is shown in figure 7.2 and the assignments are listed in table 7.2.

ii) $(\text{CH}_3)_2\text{AlH}$, $(\text{CH}_3)_2\text{AID}$, and $(\text{CD}_3)_2\text{AlH}$ - dimethylalanes

FTIR spectra of the above three compounds in the vapour phase are shown in figures 7.3, 7.4, and 7.5 respectively. The IR and Raman spectra of these species have recently been re-investigated by Grady et al. [13], and the recorded spectra are listed in table 7.3. DMAIAlH has been extensively studied by IR, Raman, Electron diffraction and molecular weight studies by a number of workers [31-33]. In the vapour phase at
Figure 7.1: FTIR spectrum of 5 torr of (CH₃)₃Al.
TABLE 7.1: FTIR SPECTRUM OF TRIMETHYLALANE (cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>FTIR*</th>
<th>REF. [28]</th>
<th>ASSIGNMENT#</th>
</tr>
</thead>
<tbody>
<tr>
<td>2943 (s)</td>
<td>2944 (s)</td>
<td>(\nu_{as}(\text{CH}_3))</td>
</tr>
<tr>
<td>2903 (s)</td>
<td>2904 (m)</td>
<td>(\nu_{s}(\text{CH}_3))</td>
</tr>
<tr>
<td>2842 (m)</td>
<td>2845 (w)</td>
<td>(\delta_{as}(\text{CH}_3) \times 2)</td>
</tr>
<tr>
<td>1254 (m)</td>
<td>1255 (m)</td>
<td>(\delta_{s}(\text{CH}_3)_b)</td>
</tr>
<tr>
<td>1208 (s)</td>
<td>1208 (s)</td>
<td>(\delta_{s}(\text{CH}_3)_t)</td>
</tr>
<tr>
<td>777 (vs)</td>
<td>774 (s)</td>
<td>(\rho(\text{CH}_3)_t)</td>
</tr>
<tr>
<td>702 (vs)</td>
<td>700 (vs)</td>
<td>(\nu(\text{AlC}_2)_t)</td>
</tr>
<tr>
<td>653 (m)</td>
<td>650 (vw)</td>
<td>(\rho(\text{CH}_3)_t)</td>
</tr>
<tr>
<td>610 (s)</td>
<td>609 (m)</td>
<td>(\rho(\text{CH}_3)_b)</td>
</tr>
<tr>
<td>567 (s)</td>
<td>567 (s)</td>
<td>(\nu(\text{AlC}_2)_b)</td>
</tr>
</tbody>
</table>

* Vapour phase FTIR spectrum of dimeric TMA\(_1\) at 298 K.
# b=bridge and t=terminal from reference [28].
Figure 7.2: FTIR spectrum of 5 torr of (CD$_3$)$_3$Al.
<table>
<thead>
<tr>
<th>FTIR</th>
<th>REF. [27]</th>
<th>ASSIGNMENTS#$</th>
</tr>
</thead>
<tbody>
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<td>2200 (s)</td>
<td>2200</td>
<td>$\nu_{as, s}(\text{CH}_3)$</td>
</tr>
<tr>
<td>2166 (w)</td>
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<td>2110 (w)</td>
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</tr>
<tr>
<td>1139 (w)</td>
<td>1140</td>
<td>$\delta_{s}(\text{CH}_3)_t$</td>
</tr>
<tr>
<td>1038 (m)</td>
<td>1036</td>
<td>$\rho(\text{CH}_3)_b$</td>
</tr>
<tr>
<td>957 (vs)</td>
<td>955</td>
<td>$\rho(\text{CH}_3)_t + \nu(\text{AlC}_2)_t$</td>
</tr>
</tbody>
</table>

# Assignments are those of reference [27].
Figure 7.3: FTIR spectrum of 2 torr of (CH$_3$)$_2$AH.
Figure 7.4: FTIR spectrum of 2 torr of (CH$_3$)$_2$AlD.
Figure 7.5: FTIR spectrum of 2 torr of (CD$_3$)$_2$AlH.
TABLE 7.3: FTIR SPECTRA OF DIMETHYLALANE DIMERS (cm\(^{-1}\)).

<table>
<thead>
<tr>
<th></th>
<th>(CH(_3))(_2)AlH</th>
<th>(CD(_3))(_2)AlH</th>
<th>(CH(_3))(_2)AlD</th>
<th>ASSIGNMENT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2955</td>
<td>2205</td>
<td>2955</td>
<td>(\nu_{as}(\text{CH}_3))</td>
<td></td>
</tr>
<tr>
<td>2905</td>
<td>2112</td>
<td>2905</td>
<td>(\nu_s(\text{CH}_3))</td>
<td></td>
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<tr>
<td>1444</td>
<td>1036</td>
<td>1440</td>
<td>(\delta_{as}(\text{CH}_3))</td>
<td></td>
</tr>
<tr>
<td>1206</td>
<td>955</td>
<td>1204</td>
<td>(\delta_s(\text{CH}_3))</td>
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</tr>
<tr>
<td>709</td>
<td>–</td>
<td>708</td>
<td>(\rho(\text{CH}_3))</td>
<td></td>
</tr>
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<td>692</td>
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<td>708</td>
<td>(\omega(\text{CH}_3))</td>
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</tr>
<tr>
<td>#</td>
<td>#</td>
<td>–</td>
<td>(\nu_{as}(\text{Al-H}))</td>
<td></td>
</tr>
<tr>
<td>1215</td>
<td>1217</td>
<td>–</td>
<td>(\nu_s(\text{Al-H}))</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>1006</td>
<td>(\nu_{as}(\text{Al-D}))</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>905</td>
<td>(\nu_s(\text{Al-D}))</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>638</td>
<td>–</td>
<td>(\nu_{as}(\text{AlC}_2))</td>
<td></td>
</tr>
<tr>
<td>571</td>
<td>578</td>
<td>567</td>
<td>(\nu_s(\text{AlC}_2))</td>
<td></td>
</tr>
<tr>
<td>851</td>
<td>832</td>
<td>737</td>
<td>(\rho(\text{AlC}_2))</td>
<td></td>
</tr>
</tbody>
</table>

* Assignments are those of reference [13].

# Perturbed by Fermi interactions.
room temperature, DMAIH is largely dimeric, with contributions from higher species, while in solution it is mainly trimeric in structure, again with contributions from higher degrees of aggregation [13]. The purity of the DMAIH was checked by recording a $^1$H NMR spectrum at 298 K. This revealed the presence of a broad singlet, characteristic of protons bound to Al, around $\delta_H$ 3.10 ppm and a sharp singlet at $\delta_H$ -0.20 ppm due to the methyl protons. $^1$H NMR spectra for (CD$_3$)$_2$AlH and (CH$_3$)$_2$AlD were also recorded in order to confirm the absence of (CD$_3$)$_3$Al and (CH$_3$)$_3$Al respectively.

7.3.3 Sample Preparation

i) Gas Phase FTIR Study

The vapour pressure of the dimethylalane or one of its isotopomers (which is in the order of 2.00 torr at 298 K) was introduced into the reaction cell first. This was then followed by the addition of an overpressure of trimethylalane, i.e. >4 torr, such that, on briefly opening the cell to the line the pressure throught out the cell dropped to ~4 torr. In order to achieve the required ratio of reactants, it was often necessary to add a further pressure of trimethylalane. This method does not take into account the fact that species might be lost from the gas phase, resulting in a decrease in the pressure inside the cell. Therefore the stated ratios can only be regarded as an approximate guide.

ii) $^1$H NMR Study

Samples for NMR spectroscopy were prepared by mixing the components in the gas phase as above, followed by condensation and addition of out-gassed, fully dried, solvent at 77 K. Spectra in d$_8$-toluene were referenced to the Me-protonated impurity of the solvent at $\delta_H$ 2.10 ppm, and those in cyclopentane to the solvent at $\delta_H$ 1.50 ppm. Variable temperature spectra were recorded with an estimated accuracy of 1-2 K.
iii) Liquid Phase FTIR Study
A 1:1 mixture of DMAIH and TMAI was prepared first in the gas phase; this was then condensed into a sample tube, followed by the addition of excess cyclopentane.

iv) Apparatus
The equipment used was described in Chapter 2. All experiments were carried out using the reaction cell illustrated in figure 2.3. Liquid phase spectra were recorded at high dilution with a path length of 12 μm, also using ZnSe windows for direct comparability.

7.4 FTIR Study of Exchange Reactions in the Gas Phase
7.4.1 DMAIH + TMAI

Figure 7.6 shows FTIR spectra of mixtures of fully protonated DMAIH and TMAI. In all spectra, only the region between 2000 and 500 cm$^{-1}$ is shown because the region above 2000 cm$^{-1}$ contains only uninformative CH$_3$ (or CD$_3$) stretching vibrations, and the cut-off of the ZnSe window material prevents meaningful measurements below 500 cm$^{-1}$. Spectrum 7.6A is a computer co-addition of the pre-recorded spectra of the two individual components, and spectrum 7.6B is that of a 1:1 mixture of the two. It is readily apparent from an inspection of these two spectra that the mixture contains very different species from the two starting materials, as some features which are uniquely assignable to DMAIH or TMAI are almost indetectable in this mixture. The most significant changes are firstly the loss of the strong broad peak at 1789 cm$^{-1}$, ascribed to the Al-H-Al asymmetric stretching mode in trimeric DMAIH; this is replaced by two weaker and narrower peaks between 1500 and 1600 cm$^{-1}$. Secondly, but of more significance, is the replacement of the characteristic doublet at 851 cm$^{-1}$, (AlMe$_2$ rocking vibration in dimeric DMAIH) by an even stronger similar doublet feature at 815 cm$^{-1}$. A similar band was also observed in both the FTIR spectra of a mixture of DMAIH + DMAID [13], and in the IR LPHP of DMAIH by Grady [12]. In both cases it was assigned to the Me$_2$Al rocking
Figure 7.6: Gas phase FTIR spectra of mixtures of (CH$_3$)$_2$AlH and (CH$_3$)$_3$Al. A = computer co-added spectra; B = spectrum of 1:1 mixture; C = spectrum of 1.6:1 mixture after computer subtraction of excess (CH$_3$)$_2$AlH. The peaks marked (●), (▲), and (■) are those assigned to vibrations fitted in the normal coordinate analysis.
vibration in a dimeric mixed bridged species, Me₂Al(μH)(μX)AlMe₂, where X=D or F. Other less clearly defined changes were observed between 1200 and 1450 cm⁻¹, in the region of the Al-H stretches in dimeric DMAIH, and also in the Al-C stretching and Me rocking modes around 800 cm⁻¹. In order to obtain a clearer picture of the changes produced, a spectrum was recorded of DMAIH and TMAI in the ratio 1.6:1; this was followed by the subtraction of excess DMAIH using the clear peak at 851 cm⁻¹ as a guide. This resulted in the spectrum shown in figure 7.6C.

### 7.4.2 DMAID + TMAI

Figure 7.7 shows a 1.6:1 mixture of (CH₃)₂AlD and (CH₃)₃Al, after features due to excess DMAID have been subtracted out. In this system both the symmetric Al-D stretch (at 1006 cm⁻¹) and its asymmetric counterpart (905 cm⁻¹) are replaced by similar bands at slightly higher wavenumber (1038 and 994 cm⁻¹ respectively); this was accompanied also by the disappearance of the asymmetric Al-D stretching mode in trimeric DMAID at 1280 cm⁻¹. This is coupled with a shift in the Me₂Al rocking vibration from 737 cm⁻¹ (in dimeric DMAID) to 758 cm⁻¹, which makes this new peak mid-way between the methyl rocking vibrations in DMAID and TMAI.

### 7.4.3 d₆-DMAIH + d₉-TMAI

Figure 7.8 shows a 1.6:1 mixture of (CD₃)₂AlH and (CD₃)₃Al, in which excess d₆-DMAIH has been subtracted out for extra clarity. The most prominent changes are again the loss of the asymmetric Al-H stretching vibration in trimeric (CD₃)₂AlH at 1790 cm⁻¹, which seems to have been replaced by a narrower peak at 1513 cm⁻¹. While in the region 1600-1200 cm⁻¹ features due to dimeric (CD₃)₂AlH are replaced by two new peaks at 1411 cm⁻¹ and 1352 cm⁻¹ respectively. These are ascribed to the asymmetric and symmetric stretching modes of Al-H in a dimeric mixed bridged species. The Me₂Al rocking vibration in accord with this shifts from 832 cm⁻¹ to 784 cm⁻¹. Table 7.4 summarizes the Al-H stretching and the Me₂Al rocking

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Figure 7.7: Gas phase FTIR spectrum of a 1.6:1 mixture of (CH$_3$)$_2$AlD and (CH$_3$)$_3$Al after computer subtraction of excess (CH$_3$)$_2$AlD. The peaks marked (○), (▲), and (■) are those assigned to vibrations fitted in normal coordinate analysis.
Figure 7.8: Gas phase FTIR spectrum of a 1.6:1 mixture of (CD$_3$)$_2$AlH and (CD$_3$)$_3$Al after computer subtraction of excess (CD$_3$)$_2$AlH. The peaks marked (●), (▲), and (■) are those assigned to vibrations fitted in normal coordinate analysis.
TABLE 7.4: Al-H STRETCHING AND Me₂Al ROCKING VIBRATIONS IN BRIDGED SYSTEMS.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>VIBRATION</th>
<th>OBSERVED</th>
<th>CALCULATED</th>
<th>OBSERVED IN DMAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃, H</td>
<td>ν_{as}(AlH)</td>
<td>1416</td>
<td>1416</td>
<td>1353</td>
</tr>
<tr>
<td>CH₃, H</td>
<td>ν_{s}(AlH)</td>
<td>1339</td>
<td>1345</td>
<td>1215</td>
</tr>
<tr>
<td>CH₃, H</td>
<td>ρ(AlMe₂)</td>
<td>815</td>
<td>803</td>
<td>851</td>
</tr>
<tr>
<td>CD₃, H</td>
<td>ν_{as}(AlH)</td>
<td>1411</td>
<td>1415</td>
<td>e</td>
</tr>
<tr>
<td>CD₃, H</td>
<td>ν_{s}(AlH)</td>
<td>1352</td>
<td>1345</td>
<td>1217</td>
</tr>
<tr>
<td>CD₃, H</td>
<td>ρ(AlMe₂)</td>
<td>784</td>
<td>793</td>
<td>832</td>
</tr>
<tr>
<td>CH₃, D</td>
<td>ν_{as}(AlD)</td>
<td>1038</td>
<td>1032</td>
<td>1006</td>
</tr>
<tr>
<td>CH₃, D</td>
<td>ν_{s}(AlD)</td>
<td>994</td>
<td>995</td>
<td>905</td>
</tr>
<tr>
<td>CH₃, D</td>
<td>ρ(AlMe₂)</td>
<td>758</td>
<td>757</td>
<td>737</td>
</tr>
</tbody>
</table>

a. CH₃, H = (CH₃)₂Al(μCH₃)(μH)Al(CH₃)₂, etc.
b. ν=stretch, ρ=rock, s=symmetric, as=asymmetric.
c. From reference [13].
d. In (CH₃)₂Al(μH)(μD)Al(CH₃)₂.
e. Perturbed by Fermi resonance.
f. In (CH₃)₂Al(μD)₂Al(CH₃)₂.
vibrations in the above three mixed bridged systems.

7.5 FTIR Study of Exchange Reactions in Solution

7.5.1 DMAIH + TMAI in Cyclopentane

Figure 7.9 illustrates the liquid phase FTIR spectrum of a 1:1 mixture of DMAIH and TMAI in cyclopentane solution. In DMAIH itself, the position of equilibrium between dimeric and higher oligomeric forms is considerably shifted in solution. On comparison with figure 7.6B it can be seen here that the peak at 808 cm⁻¹, corresponding to the dimeric form of the mixed bridged species is much weaker, and is therefore less dominant than in the gas phase mixture. Again in complete contrast in the gas phase spectra is the observation of a strong asymmetric stretch at ~1800 cm⁻¹, ascribed to Al-H in the trimeric mixed bridged species. Further more there is no evidence of the presence of either the methyl rocking vibration at 851 cm⁻¹, due to dimeric DMAIH or the mixed trimer peaks at 1500 cm⁻¹. However, in toluene solution the NMR measurements taken correlate closely with the composition of the mixture in the gas phase.

7.6 ¹H NMR Study of Exchange Reactions in Solution

7.6.1 DMAIH + TMAI in d₈-Toluene

Figure 7.10 shows the ¹H NMR spectrum at 191 K (at lower temperatures the solution becomes a glass) of an approximately 1:1 molar ratio (based on Al content) of DMAIH and TMAI. In the region where Al-H resonances occur, two strong broad peaks at δₜ 2.65 ppm (B) and δₜ 3.64 ppm (A) are observed in an integrated ratio of approximately 5:1. The former of these is ascribed (on the basis of comparison with the spectrum of pure DMAIH) to DMAIH in its normal trimeric or higher form; the latter peak is assigned to the dimeric crossed bridged species on the basis of the IR spectra recorded. In some of the spectra an additional weaker resonance at δₜ 3.16 ppm (C) was observed; this is ascribed to a trimeric mixed bridged species.
Figure 7.9: Liquid phase FTIR spectrum of a 1:1 mixture of (CH$_3$)$_2$AlH and (CH$_3$)$_3$Al in cyclopentane solution, after computer subtraction of solvent features (the features marked * arise from imperfect subtraction).
Figure 7.10: $^1$H NMR spectrum of a 1:1 mixture of (CH$_3$)$_2$AlH and (CH$_3$)$_3$Al in d$_8$-toluene at 191 K. Only the regions of Al-H and Me resonances are shown; features marked (*) are assigned to impurities. A, B, and C are assigned to Al-H resonances, and D-G to Me resonances as discussed in section 7.6.1.
However, the region of the methyl resonances is more complicated. In addition to the terminal ($\delta_H -0.52$ ppm, E) and bridging ($\delta_H 0.03$ ppm, D) methyl groups of TMAI, and the methyl groups of DMAIH ($\delta_H -0.14$ ppm, F), there is an additional broader peak in the terminal methyl region at $\delta_H -0.48$ ppm, (G), plus a number of weak, sharp features. The new broad feature (G) can be assigned to the terminal methyl group of the mixed bridged species; the sharper features are thought to originate either from impurities or higher oligomeric units in DMAIH [34].

At higher TMAI to DMAIH ratios, the intensities of both the Al-H and Me resonances ascribed to the mixed bridged species increase relative to those of DMAIH. Figure 7.11 illustrates the spectra recorded for the 1:1 mixture of DMAIH and TMAI as the temperature is gradually raised. In the methyl region (A), as the temperature is raised above 200 K, the peak assigned to the mixed bridge species broadens and disappears. Around 220 K, the bridging and terminal peaks of TMAI broaden and coalesce, and reappear in the fast exchange regime around 250 K; this is very similar to the classic observations of this species alone reported as long ago as the 1950’s [14]. Finally, the DMAIH methyl resonance broadens above 270 K, and by 300 K all Me groups are apparently in rapid exchange. The dramatic variations in line widths over this temperature range, coupled with the overlap of many of the features, prevented any analysis of the change in the relative proportions of the species present.

In the region of the Al-H resonances (B) the situation is quite different. Here between 191 and 290 K broadening is relatively modest; on the other hand, the relative integrated intensities of the two peaks shift in favour of the crossed bridge species, so that at temperatures above 280 K, it is the greater of the two. Above 300 K, the two species evidently undergo exchange with coalescence of the two peaks around 325 K. $^{13}$C NMR spectra were recorded for this system, but unfortunately only resonances assignable to the starting materials could unambiguously be detected.
Figure 7.11: $^1$H NMR spectra of a 1:1 mixture of (CH$_3$)$_2$AlH and (CH$_3$)$_3$Al in d$_8$-toluene between 191 K and 361 K in the Me (A) and Al-H (B) regions. Peak heights at each temperature are normalised to the strongest in each region (which may actually correspond to a narrow impurity feature, marked ●, in some cases). Note the different scales of A and B.
7.6.2 DMAIH + TMAI in Cyclopentane

It is well known that exchange processes involving Al-bound alkyl groups in cyclopentane solution are slower than in toluene, and therefore $^1$H NMR spectra were recorded in this solvent. Unfortunately, in this case the equilibrium is considerably shifted away from the mixed bridge species, as was indicated by the solution IR study in section 7.5.1, and by the ratio of the integrated intensities of the Al-H resonances. Despite the fact that a weaker and sharper additional terminal resonance was observed, the quality of the spectrum in the bridging methyl region precluded any further investigation.

7.7 Discussions and Conclusions

The gas phase IR observations leave little doubt that the predominant species in the gas phase is the mixed bridged dimeric species, Me$_2$Al(μH)(μMe)AlMe$_2$, with smaller contributions from trimeric or higher species with both H and Me bridging units. Although the presence of these species is not surprising, the extent of the dominance of the mixed dimer is somewhat unexpected, and it is of interest to enquire into its origin. In the exchange equilibria

$$\text{TMAI}_2 + \text{DMAIH}_2 \rightarrow 2X_2$$ \hspace{1cm} [7.7]

$$3\text{TMAI}_2 + 2\text{DMAIH}_3 \rightarrow 6X_2$$ \hspace{1cm} [7.8]

with the degree of association of trimethylalane (TMAI) and dimethylalane (DMAIH) indicated by subscripts, and $X_2$ representing the mixed bridge dimer, formation of $X_2$ is entropically slightly favoured in [7.8], and approximately neutral in [7.7]. It follows that formation of $X_2$ in [7.7] must be energetically strongly favourable, and hence that the Al-H-Al bridging bond in the mixed dimer is stronger than that in the homo-bridged dimer.

The $^1$H NMR results provide strong support for the above conclusions. The observation of two major Al-H resonances readily ascribed to the dominant dimeric mixed bridge and trimeric dimethylalane units is similar to that of Eisch and Rhee in...
the isobutyl case [23]. It is also of interest to mention that the IR LPHP of DMAIH can lead to the production of the dimeric mixed bridge species described above [12].

Normal coordinate analysis (NCA) carried out by Russell [35] of the vibrations of the mixed bridge species revealed that the force constant of the Al-H-Al bridging bond is stronger in the mixed bridged species, while the force constant of the Al-Me-Al bond is weaker in the mixed dimer, see table 7.5. Ab initio calculations carried out by Claxton [35]; the results of which are shown in table 7.6, fully support the NCA results. Recently, far-infrared spectra of gas phase mixtures of TMAI and DMAIH were recorded by Mahmood [36]; which showed that the Al-Me-Al bridging bond is shifted to lower frequency. In all respects, this additional data provided further evidence to support all the conclusions drawn from the experimental observations. In that the replacement of one of the bridging H atoms in the Al(μH)₂Al by a less strongly electron-withdrawing Me group leads to a marked strengthening of the remaining Al-H-Al bridge. This manifests itself in an increase in the vibrational frequency, and a decrease in the rate of the exchange process.
TABLE 7.5: FORCE CONSTANTS IN H-BRIDGED ALANES.

<table>
<thead>
<tr>
<th>FORCE CONSTANT$^a$</th>
<th>IN MIXED BRIDGE</th>
<th>IN DMA1H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-H$_b$ stretch</td>
<td>1.07$^b$</td>
<td>0.96$^c$</td>
</tr>
<tr>
<td>Al-H$_b$/Al-H$_b$ stretch/stretch</td>
<td>0.16$^b$</td>
<td>0.09$^c$</td>
</tr>
<tr>
<td>Me$_t$-Al-H$_b$ bend</td>
<td>0.28$^d$</td>
<td>0.26$^c$</td>
</tr>
</tbody>
</table>

$^a$ b = bridge, t = terminal $^b$ mdyne Å$^{-1}$ $^c$ from ref.[13]. $^d$ mdyne Å rad$^{-2}$. 
### TABLE 7.6: Ab Initio Calculations For H-bridged Alanes.

<table>
<thead>
<tr>
<th></th>
<th>$\text{Al}_2\text{H}_6$</th>
<th>$\text{Al}_3\text{H}_9$</th>
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</thead>
<tbody>
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<td>173.0</td>
</tr>
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<td>146°</td>
<td>99°</td>
</tr>
<tr>
<td>$v_{as}(\text{Al-H}_b$-$\text{Al})$/cm$^{-1}$</td>
<td>1545</td>
<td>–</td>
<td>1566</td>
</tr>
<tr>
<td>$v_{s}(\text{Al-H}_b$-$\text{Al})$/cm$^{-1}$</td>
<td>1321</td>
<td>–</td>
<td>1478</td>
</tr>
<tr>
<td>$H_b$ atomic charge</td>
<td>-0.264</td>
<td>-0.323</td>
<td>-0.254</td>
</tr>
<tr>
<td>a. $\text{H}_2\text{Al}(\mu\text{H})(\mu\text{Me})\text{AlH}_2$</td>
<td></td>
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REFERENCES


T. A. Claxton, to be published.

Chapter Eight

Conclusions
The pyrolysis studies presented in this thesis have shown that using the technique of IR LPHP a better insight into the mechanisms of gas phase reactions can be achieved, particularly in terms of the trapping and isolation of both short-lived intermediates and primary reaction products. However, the disadvantages of this technique are firstly, that precise temperatures cannot be defined in the reaction cell, and secondly, that it is rather difficult to relate gas phase mechanisms to growth mechanisms in MOVPE reactors, where of course heterogeneous contributions are much greater. In the future, it is hoped that precise kinetic parameters will be determined using stir-flow reactors on the chemical systems presented here, and that ESR studies using conventional hot-tube pyrolysis and laser pyrolysis will permit the disentangling of homogeneous and heterogeneous contributions in MOCVD.

The IR LPHP of TEGa + TMGa mixtures is very interesting in the further light it sheds on alkyl group exchange reactions in the gas phase and also how the \( \beta \)-hydride elimination pathway may be used to selectively remove ethyl groups. Without the use of the Lewis base, NMe\(_3\), to form adducts with the pyrolysis products, the identification of the numerous species in both the gas phase and in \( d_8 \)-toluene solution would have been impossible. The IR LPHP of TIPGa, TIBGa, and TTBGa was revealing in that it demonstrated how both the alkyl group size and the amount of branching affect the extent of the competition between the \( \beta \)-hydride elimination and the bond homolysis pathways. Again the use of NMe\(_3\) greatly helped in terms of both the ease of identification and prolonging the stability of the dialkylgallanes. The results of Chapter 4 also correlate well with the spectroscopic surface growth studies of Foord and co-workers, as previously described. From the results presented here for the laser pyrolysis of trialkylgallanes, it can be concluded that TMGa decomposes via a radical bond homolysis route, and for the higher trialkyls as the size of the alkyl group increases so does the ease with which \( \beta \)-elimination can take place.

The results of the laser pyrolysis of TEB are somewhat disappointing, however, the great strength of the B-C bond coupled with the complex chemistry of
organoboron compounds can go some way in explaining the rather inconclusive observations. It is hoped that future work on the TEB system using conventional hot-tube pyrolysis and ESR matrix isolation will provide a greater insight into the predominant reaction mechanism. For the TEIn system where the bond homolysis mechanism dominates, this result is an extremely good example of how the stabilities of the Group III trialkyls differ on descending the group. It can therefore be concluded that the first two members of the Group III triethyl compounds: TEB and TEAl were difficult to study due to perhaps complex chemistry in the former case and low volatility in the latter, while TEGa pyrolyses entirely via a clean β-hydride elimination mechanism and TEIn decomposes exclusively via a mechanism involving free radicals to deposit indium metal.

The laser pyrolysis of DEZn is the best example to date of the distinct advantage the IR LPHP technique offers in terms of trapping the primary reaction products, in this case ZnH$_2$. In particular the DEZn system proves the dangers of deducing reaction mechanisms from the final reaction products. Future work will be centred around investigating the decomposition of higher alkyls of zinc, in order to see the extent to which the β-hydride elimination mechanism predominates and also the laser pyrolysis of analogous compounds such as diethyl cadmium is to be carried out. It is hoped to eventually compare the trends in the Group II dialkyls with those of the Group III trialkyl compounds. Finally it is hoped that X-ray photoelectron spectroscopy may be used to analyse the deposited ZnH$_2$.

Gas phase exchange studies have been shown to be extremely useful in gaining an understanding of the mechanisms of the MOVPE growth process, as was clearly illustrated in the FTIR study of TMAA + TMGa and TMAA + TEGa mixtures. For mixtures of DMAIH + TMAI it was shown spectroscopically that the properties of the mixture were not simply those of the initial components. It was clearly shown by both gas phase FTIR and solution NMR that on mixing DMAIH with TMAI the predominant species is a mixed hydrogen-methyl bridged dimer,
$\text{Me}_2\text{Al}(\mu\text{H})(\mu\text{Me})\text{AlMe}_2$. It is of significance however, that the formation of this mixed bridged species is not the sole reason for the difference in proton chemical shifts from those of the initial species. Previous classical solution studies have unfortunately tended to base their conclusions on the ratios of the integrals of the concentrations of the components, rather than to the changes in molecularity i.e. from trimeric to dimeric. Future work on the DMAIH and TMAI system will involve mass spectrometric studies of different ratios of the two species.

The main contributions of this thesis to the MOVPE growth of compound semiconductors are that simpler parts of the overall growth process have been investigated e.g. the pyrolysis of TEIn alone rather than with AsH$_3$; by this method a better understanding of precise mechanisms can be achieved. Finally the application of novel spectroscopic techniques such as IR LPHP with its particular advantages over conventional methods have been used to successfully tackle problems of structure.