

## Spectroscopic Studies of Exchange and Pyrolysis Reactions in Mixtures of Trimethylamine alane, Trimethylgallane and Triethylgallane

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**Summary:** Rapid alkyl exchange reactions in gas phase mixture of trimethylamine alane and trialkylgallane lead to a statistical mixture of trialkylgallane. Partial pyrolysis of these mixtures leads to selective  $\beta$ -elimination of ethyl groups, resulting in a mixture of dialkyl and monoalkylgallanes, which have been characterised by FTIR, proton NMR and mass spectrometry. The mass spectrometric observations reveal the presence of dimeric and trimeric species. The NMR results confirm this conclusion, and further suggest that intermolecular exchange processes are fast even at 200 K, whereas intermolecular exchange is significant only above 250 K.

### Introduction

The trialkyls of group III elements have been extensively used in 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, while 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, such as  $\text{EtMe}_2\text{In}$ , which could combine the high volatility of the methyl compounds with the reduced carbon incorporation of the ethyl compounds.

The indium precursor,  $\text{EtMe}_2\text{In}$ , which is liquid at room temperature, was first used to grow GaInAs film in an atmospheric pressure MOVPE reactor. In that work [4,5], the formation of extremely poor quality layers was reported. An alternative aluminium precursor,  ${}^t\text{BuMe}_2\text{Al}$ , was used by Jones *et al.* [6] to grow AlGaAs in an atmospheric pressure MOVPE reactor. It was thought that the presence of a 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  ${}^t\text{BuMe}_2\text{Al}$  may decompose in the reactor prior to growth, yielding dimethylalane, DMAIH, and that although deposited layers of AlGaAs of good optical quality were grown, the level of the carbon contamination was

approximately equal to that using TMAI. On the positive side, however, it was concluded that  ${}^t\text{BuMe}_2\text{Al}$  did show potential for high quality aluminium growth at low substrate temperatures.

On the other hand, ethyl-based materials are subject to the facile elimination of ethyl groups by the  $\beta$ -elimination process on pyrolysis [7] which leads to a much cleaner deposition of the desired metal. As a result, Al and AlAs films with no detectable carbon have been grown using TEAl and  $\text{Et}_2\text{AlH}$  as aluminium precursors [8-11]. However only limited success has been achieved in the growth of AlGaAs in combination with TMGa. By replacing TMGa with TEGa, AlGaAs layers with no detectable carbon can be grown using TEAl [8]. However, TEAl is thermally less stable than TEGa, with the result that the Al content of the alloy decreases in the downstream direction. The extremely low vapour pressure of TEAl requires the heating of reactor lines and sources, which often leads to the decomposition of the compounds in the reactor lines and poor growth rates [12].

Even a compound that contains no bonds to carbon *i.e.* TMAA, has shown no advantage over TMAI when used in combination with TMGa. Again, this is despite the use of TMAA as a precursor to high purity aluminium by chemical vapour deposition [13]. However, on replacement with TEGa, AlGaAs layers with no detectable carbon can be grown at all compositions. TMAA also has a much higher vapour pressure than TEAl and thus, of the alternative materials studied, this compound appears to be most promising.

Clearly, the source of carbon in AlGaAs layer grown using ethyl and hydride based (*i.e.* TMAA) Al-precursors, must be TMGa, yet low carbon-content GaAs layers can be grown with this compound. Furthermore, the thickness uniformity of the AlGaAs layers were generally poor, with the direction of increasing Al content in the alloys being in the opposite direction to that expected from the thermal stabilities of the precursors used, *i.e.* the aluminium content of the alloy often increased in the downstream direction. It would seem probable, therefore, that gas-phase reactions transferring ligand groups, and thus forming new molecules with differing thermal stabilities, are responsible, a hypothesis born out by evidence of deposition on the reactor inlet.

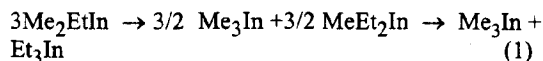
Ligand exchange reactions between Al and Ga alkyls have been widely studied in solution [14] but very little is known about the extent of these reaction in the gas-phase. To date, only mixtures of TMAI and TEGa have been studied and the methyl-ethyl exchange products formed in gas phase have been identified [15].

The main objective of this work was to investigate the alkyl group exchange reactions for tri-alkylgallium compounds (TMAA/TMGa, and TMGa/TEGa) at room temperature and low temperatures using FTIR,  $^1\text{H}$  NMR and mass spectroscopies. Also, the IR LPHP of triethylgallium (TEGa) and trimethylgallium (TMGa), mixture was investigated. This work showed that the technique of IR LPHP not only give unambiguous evidence for the  $\beta$ -elimination pathway, but also provides a route to diethyl and monoethylgallanes. The aim of this was to selectively  $\beta$ -eliminate the ethyl groups, thus providing a synthetic route to dialkylgallane and the novel mono-alkylgallane.

#### *Synthesis and Properties of Mixed Alkyl Group Compounds.*

Bradley and co-workers have recently reported the synthesis of the compounds  $\text{Me}_2\text{EtM}$  and  $\text{Me}_2\text{EtM.NMe}_3$  where  $\text{M}=\text{Al}$  or  $\text{In}$  [16]. These heteroleptic alkyls were prepared by reacting  $\text{Me}_2\text{MCl}$  with  $\text{EtMgBr}$  in diethylether, followed by the formation of adducts with diphos  $(\text{Ph}_2\text{PCH}_2)_2$ . The white crystalline solids produced were then heated to 353 K, whereupon colourless distillates of  $\text{Me}_2\text{EtAl}$  and  $\text{Me}_2\text{EtIn}$  formed. Variable temperature  $^1\text{H}$  NMR spectra for both compounds revealed that rapid alkyl group exchange occurs and for  $\text{Me}_2\text{EtIn}$

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  $\text{Me}_3\text{In}$ , which is in agreement with the proposed disproportionation reaction in solution:



It was the opinion of these workers [16] that the compounds formulated as  $\text{Me}_2\text{EtAl}$  and  $\text{Me}_2\text{EtIn}$  are not suitable precursors for MOVPE/MBE of III-V materials as the alkyl groups are too labile.

Barron and Cleaver [17] have prepared hybrid organometallic compounds of gallium like  $^t\text{Bu}_2\text{MeGa}$  and  $^t\text{BuMe}_2\text{Ga}$  by the reaction of alkylating agents methyl lithium with a halogenated organogallium compounds in hexane. These compounds 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 [18].

Agnello and Ghandhi have studied the room temperature gas phase exchange reaction between TMGa and TEIn [19]. The experiment were carried out in a conventional low pressure MOVPE reactor and the reaction was monitored using mass spectrometry. From this work Agnello *et al.* conclude that TMGa and TMIIn not only form an adduct 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  $\text{Me}_2\text{In}^+$  and  $\text{Et}_2\text{Ga}^+$ , coupled with a reduction in the Me-Ga and Et-In peaks. Signals attributed to  $\text{EtMe}_2\text{Ga}^+$ ,  $\text{MeEt}_2\text{Ga}^+$  and  $\text{EtMe}_2\text{In}^+$  species were also recorded. A dynamic structure was proposed for 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 TMIIn and TEGa.

A similar experiment was used to study a mixture of TEGa and TMAI using  $\text{H}_2$  as a carrier gas by Mashita *et al.* [20]. New species were found 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 MeGa on the surface.

Early studies of the pyrolysis of  $R_3M$  ( $R=Me$ ,  $Et$ ,  $M=Al$ ,  $Ga$ ,  $In$ ) were dominated by the identification of hydrocarbon products and the determination of kinetic parameters for the disappearance of starting materials. For example, for the widely-used Ga precursor triethylgallium,  $Et_3Ga$ , extensive analysis of the hydrocarbons produced (largely ethene, ethane and butane) by pyrolysis between 450 and 750 K have been carried out, [21-23] and Paputa and Price have determined the activation energy for the process using a toluene carrier system [24]. Opinion seems to have been fairly evenly divided over the predominant mechanism, with argument for both a Ga-Et radical homolysis pathway and an intramolecular  $\beta$ -elimination of ethene. Similar studies have been devoted to the alternative Ga source trimethylgallane,  $Me_3Ga$ : here of course the  $\beta$ -elimination route is not available, and the major reaction pathway undoubtedly involves Me radicals [25,26]. Radical species have recently been identified as the likely culprit in the contamination of Ga (and Al) by unwanted carbon reducing the usefulness of trimethylgallane as a Ga deposition precursor. On the other hand, the vapour pressure of trimethylgallane is considerably higher than that of triethylgallane, making it a more convenient source in high pressure processes. For these reasons, alluded to briefly in the previous section, there has been some interest in mixed alkyl species, hoping that they would combine the advantages of the greater volatility of the methyl compounds with the molecular decomposition route available for higher alkyl groups. More recently, experiments have been conducted under condition closely resembling those of Metal Organic Chemical Vapour Deposition (MOCVD) or Metal Organic Molecular Beam Epitaxy (MOMBE), with a shift in the focus of attention to the nature of the deposited material [27,28].

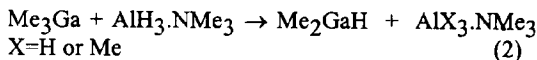
## Results and Discussion

### *Exchange Studies in Mixtures of TMGa and TMAA.*

#### *Synthesis of $Me_2GaH$ .*

Dimethylgalliumhydride was prepared from reaction between trimethylgallium (TMGa) and trimethylaminealane (TMAA). Evidence from FT IR

and NMR spectra of products showed that this procedure in accordance with the following equation.



Hence the reaction is analogous to that used for the synthesis of dimethylalane  $[Me_2AlH]_n$  from lithiumaluminiumhydride and trimethylaluminium [29].

The procedure employed was as follows. TMAA was introduced into the sample tube at  $-196^\circ C$ , an excess of TMGa was condensed in the same tube and the reaction mixture was allowed to warm up to room temperature. The reaction vessel was allowed to stand for 15 minutes at room temperature before all the volatile materials were pumped through traps maintained at  $-40^\circ C$  and  $-196^\circ C$ . This led to collection of little material at  $-196^\circ C$  but yielded about 100 mg of a solid in the trap held at  $-40^\circ C$ . The unchanged trimethylgallium passed through the trap at  $-40^\circ C$  to be retained by that at  $-196^\circ C$ . Typically, the fraction collected at  $-40^\circ C$  was a white waxy solid which melted at  $3-5^\circ C$ , at this temperature a small quantity of other volatile materials were also condensed which were pumped out by warming the sample to room temperature leaving nearly pure dimethylgalliumhydride.

### *FTIR Spectra of TMAA:TMGa Mixtures.*

Mixtures of TMAA and TMGa in the ratio 1:1 to 1:3 have been studied, at room temperature, by FTIR spectroscopy. Figure 1 shows spectra ( $500-2000\text{ cm}^{-1}$ ) for these two ratios. The region of the  $CH_3$  stretches near  $3000\text{ cm}^{-1}$  have been omitted as it was heavily overlapped by the vibration of the  $NMe_3$  moiety and provided no additional information. Clearly, these mixtures contain species other than the two starting constituents: indeed, over the range of compositions studied, no trace of TMAA was observed, and absorption due to TMGa was only observed at ratios 1:3 (Al:Ga) and greater. The reactions leading to the formation of these new species were completed within the time scale of mixing and spectrum acquisition (1-2 min). These new species may readily be attributed to the products of gas phase exchange reactions between the two starting materials.

It is very evident from figure 1(A) and 1(B) that the composition of the mixture was strongly

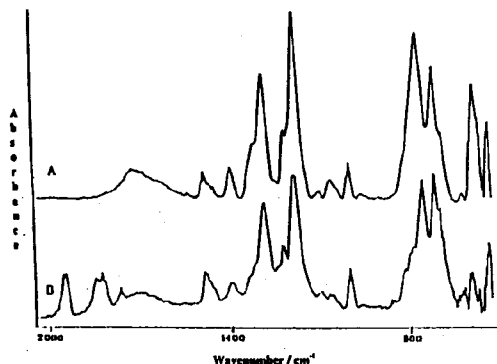


Fig. 1: FTIR spectrum of mixture of TMAA and TMGa in the ratio 1:3 (A) and 1:1 (B).

dependent on the initial component ratio. In the mixture rich in TMGa, figure 1(A), the most prominent infrared lines are readily attributed to free dimethylgallane,  $\text{Me}_2\text{GaH}$ : this species has recently been shown to exist in the gas phase as a mixture of a hydrogen-bridged trimer (with broad infrared absorption at  $1700\text{ cm}^{-1}$ ) and a dimer (stronger, narrow bands at  $1290$  and  $1185\text{ cm}^{-1}$ ) [30]. Other bands closely matching those of the trimethylamine adduct of TMAI,  $\text{Me}_3\text{Al.NMe}_3$  [31], may also be discerned from the spectrum, although they are much weaker and overlapped in many places by the dimethylgallane features

Infrared spectra of a purified sample of  $\text{Me}_2\text{GaH}$  in the vapour phase have also been recorded. The results are illustrated in figure 2 and the band positions and their assignment are

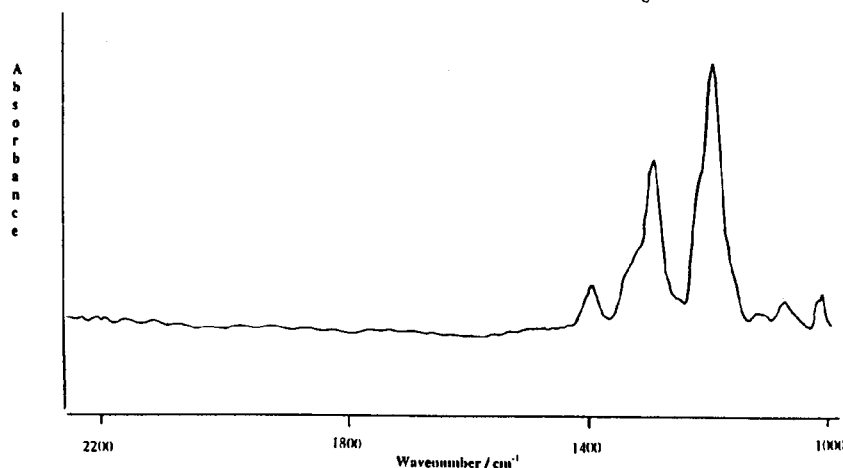


Fig. 2: FTIR spectrum of DMGaH produced by mixture of TMAA and TMGa in the ratio 1:3

summarised in table 1. The instability and reactivity of dimethylgallane made it impossible in practice to eliminate all impurities. In spite of these impurities the spectra can be interpreted satisfactorily and most of the bands can be identified with fundamentals which approximate to internal motion of the  $\text{Me}_2\text{Ga}$  group [32,33]. The absorptions at  $765$  and  $720\text{ cm}^{-1}$  correspond to  $\text{GaH}_3.\text{NMe}_3$ , reported by Green *et al.* [34], and the features near  $2980$ ,  $2919$  and  $1396\text{ cm}^{-1}$  are ascribed to  $\text{Me}_2\text{AlH.NMe}_3$  in light of the similar features found in IR spectra of dimethylgallium tetrahydroborate [33] and found by Grady *et al.* in mixture of TMAA and TEGa [35]. Impurities apart, the spectra gave no sign of significant absorption in the region  $1800\text{--}2000\text{ cm}^{-1}$ , which is characteristic of the stretching vibrations of terminal Ga-H bonds [36]. On the other hand, the spectra of  $\text{Me}_2\text{GaH}$  vapour contains two prominent absorptions at  $1288$  and  $1183\text{ cm}^{-1}$ . The most suitable interpretation is that these represent antisymmetric and symmetric stretching vibrations of a Ga-H-Ga bridge structure [37]. Such an assignment receives strong support from the IR spectrum reported by Downs and co-workers for dimethylgallane [30,38]. In addition, samples of dimethylgallane vapour show broad and very weak absorption at  $1706\text{ cm}^{-1}$  which arises from a trimeric form of this species [30]. Hence, it appears that the dimer  $[\text{Me}_2\text{GaH}]_2$  is the predominant species in the vapour phase under our experimental conditions.

#### $^1\text{H}$ NMR Spectrum of $\text{Me}_2\text{GaH}$

The  $^1\text{H}$  NMR spectrum of dimethylgallane in a solution of  $d_8$ -toluene was recorded at room

Table 1: FTIR Spectral Data of Et<sub>2</sub>GaH (cm<sup>-1</sup>)

Et <sub>2</sub> GaH(liquid).	Et <sub>2</sub> GaH(solid)*	Assignment
2942 (s)	2944(s)	v <sub>as,s</sub> (CH)
2900(s)	2902(s)	v <sub>as,s</sub> (CH)
2865(s)	2867(s)	v <sub>as,s</sub> (CH)
2813(w)	2813(w)	Overtone
2728(w)	2730	Overtone
1642(vs,b)	1657(vs,b)	v <sub>as</sub> (GaH)
1462(m)	1462(m)	δ <sub>as</sub> (CH <sub>3</sub> )
1418((w)	1417(w)	δ(CH <sub>2</sub> )
1375(m,s)	1375(w)	δ <sub>s</sub> (CH <sub>2</sub> )
1231(m)	1231(w)	ω(CH <sub>2</sub> )
1188(s)	1191(m)	ω(CH <sub>2</sub> )
997(s)	999(m)	ρ(CH <sub>3</sub> )
950(w)	961(m)	v(CC)
937(m,s)	838(m)	v(CC)
810(w,br)		v <sub>s</sub> (GaH)
697(sh)	698(m,sh)	ρ(CH <sub>2</sub> )
660(s)	663(m)	ρ(CH <sub>2</sub> )
	563(m)	v <sub>as</sub> (GaC <sub>2</sub> )
	513(m)	v <sub>s</sub> (GaC <sub>2</sub> )

s = strong m = medium, w = weak, v = very, br = broad, sh = shoulder. \* = from reference 46.

temperature and the spectrum of the solution is depicted in figure 3. This shows two resonances; one at δ<sub>H</sub> = 3.06 is broad, whereas the other at δ<sub>H</sub> = 0.01 is sharp. The positions and relative intensities leave no doubt that the broad resonance arises from protons attached to gallium and that the sharper resonance arises from a methyl proton [30]. Other peaks in the spectrum come from impurities *i.e.* unreacted materials. The instability and reactivity of dimethylgallane make it impossible in practice to eliminate all impurities.

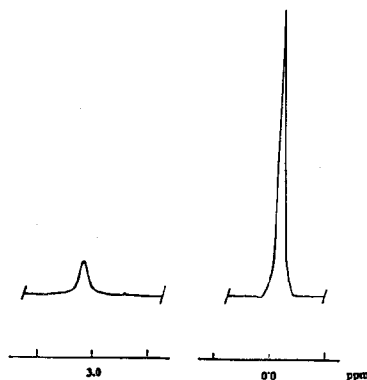


Fig. 3: <sup>1</sup>H-NMR spectrum of DMGaH in d<sup>8</sup>-toluene solution.

The fact that the spectrum is so simple means that, if more than one species is present in solution,

*e.g.* a mixture of [Me<sub>2</sub>GaH]<sub>2</sub> and [Me<sub>2</sub>GaH]<sub>3</sub>, rapid exchange must be occurring between these species. It seems more likely, however, that the predominant species is dimethylgallane in solution.

#### Synthesis of Diethylgalliumhydride by IR LPHP

IR LPHP experiments on a TEGa/SF<sub>6</sub> mixture were carried out at laser powers ranging from 1.35 to 1.50 W. Because of the inhomogeneous temperature profile, the precise temperature cannot be defined. However, a comparison with pyrolysis in systems with known kinetic parameters [39] suggest that these powers correspond to maximum temperatures in the range 500 to 750 K. The partial pressure of SF<sub>6</sub> in all cases was 10 torr, and the TEGa was condensed in the cell as required.

An FTIR spectrum obtained after exposure of 1.45 W of CO<sub>2</sub> laser radiation (after removing all the volatile materials) is shown in figure 4. Exposure to laser radiation at powers as low 1.25 W resulted in change but at a much reduced rate; TEGa appeared to be thermally stable at powers below 1.25 W. Further exposure to laser radiation led to the gradual disappearance of TEGa and the production of significant quantities of viscous liquid product and ethene. The contents of the cell were rapidly condensed into a sample tube for further analysis at 77 K (-196°C) and then pumping at 197 K in order to remove C<sub>2</sub>H<sub>4</sub> and SF<sub>6</sub>.

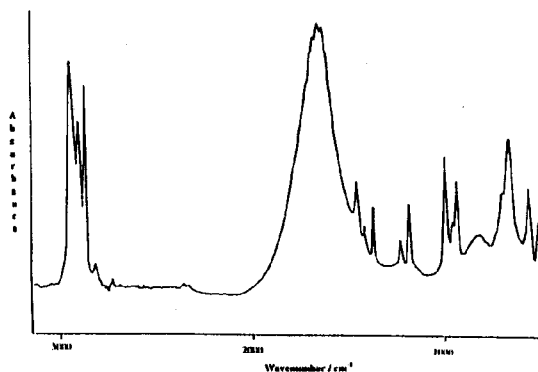


Fig. 4: FTIR spectrum of DEGaH produced by IR LPHP of TEGa.

FT IR spectra of a mixture of TEGa and SF<sub>6</sub> before and after brief IR LPHP at 1.45 W are shown in figure 5 of reference [40]. The most prominent feature of the product spectrum is the appearance of a

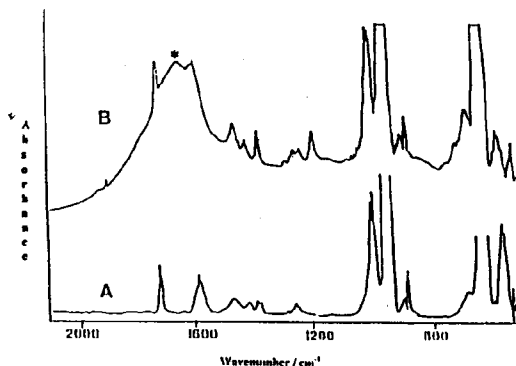


Fig. 5: FTIR spectrum of a mixture of SF<sub>6</sub> and TEGa before (A) and after (B) irradiation at 2 W of laser power for 45 second.

strong broad absorption near 1640 cm<sup>-1</sup> together with sharp peaks readily ascribed to C<sub>2</sub>H<sub>4</sub>. Examination of the pyrolysis cell revealed the presence of a liquid, and distillation from cell walls to window confirmed this liquid to be the origin of the broad absorption. The liquid product, has a relatively low vapour pressure *i.e.* 0.5 torr at room temperature. The FTIR spectrum of this product, isolated by rapidly pumping away the volatile SF<sub>6</sub> and the C<sub>2</sub>H<sub>4</sub> product is shown in figure 4, it is readily identified as that of diethylgallium hydride, DEGaH, in comparison with spectra of the similar DMGaH [30] and <sup>1</sup>BuGaH [41]. The broad absorption near 1640 cm<sup>-1</sup> is very characteristic of a Ga-H-Ga bridging bond in a trimeric ring system. Very recently, Pulham *et al.* [42] have synthesised DEGaH by the reaction of Ga<sub>2</sub>H<sub>6</sub> with C<sub>2</sub>H<sub>4</sub> at high pressure and the IR spectrum reported by them is identical with that of figure 4.

In an earlier study of TEGa pyrolysis [43], the product contained a proportion of unreacted TEGa, with which Et<sub>2</sub>GaH apparently undergoes rapid Et group exchange in solution at room temperature. Although this exchange is slowed sufficiently to permit resolution of the NMR spectra of individual components at low temperature, it does lead to some uncertainty in identification of species present. On the other hand, the pyrolysis products isolated have <sup>1</sup>H NMR spectra which showed a broad resonance at 3.07 at room temperature in d<sub>8</sub>-toluene typical of Ga-H. This is in complete accord with that of Et<sub>2</sub>GaH by Pulham *et al.* with no evidence of other organo-metallic species. Although it proved possible to produce a sample of pure Et<sub>2</sub>GaH by means of IR

LPHP, the product often contained a proportion of unreacted TEGa or further products and this complicates the interpretation of the NMR spectrum.

#### <sup>1</sup>H-NMR Spectrum of Me<sub>2</sub>GaH and Et<sub>2</sub>GaH Mixture

The <sup>1</sup>H NMR spectra of dimethylgalliumhydride and diethylgalliumhydride mixtures in a solution of d<sub>8</sub>-toluene were recorded at room temperature and also at lower temperatures. At room temperature all hydride, methyl and ethyl resonances collapse into single feature (at δ<sub>H</sub> 3.15 ppm) while at 203 K, at least five distinct Ga-H environments are identifiable in varying proportions, as indicated by the complex group of broad absorptions between δ<sub>H</sub> 2.70 and 3.00 ppm shown in figure 6(a). Ga-CH<sub>3</sub> resonances fall into two sets, a broad singlet at δ<sub>H</sub> -0.17 ppm and a complex group at between δ<sub>H</sub> 0.00 ppm and 0.25 ppm attributed to methylgallium hydrides (see figure 6(b)) and a complex overlapped cluster near δ<sub>H</sub> 0.70 ppm arising from ethylgallium hydride. Also, some resonances in the spectra may be clearly identified with homoalkylated gallanes on comparison with those identified in AlH<sub>3</sub>.NMe<sub>3</sub> mixtures with Me<sub>3</sub>Ga [44].

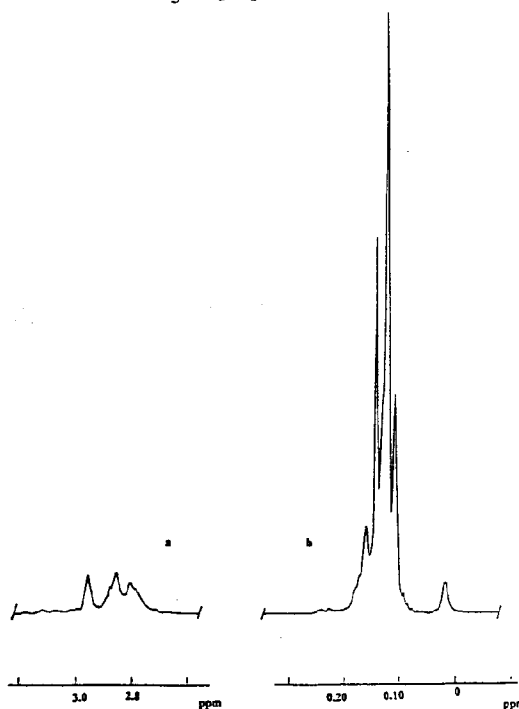


Fig. 6: <sup>1</sup>H-NMR spectrum of mixture of DMGaH and DEGaH at 203 K. Only the region of Ga-H (A) and Ga-CH<sub>3</sub> (b) resonances are shown.

### IR LPHP of TMGa+TEGa Mixtures

Laser pyrolysis of an equimolar mixtures of  $\text{Et}_3\text{Ga}$  and  $\text{Me}_3\text{Ga}$  was carried out at a laser power of 2 W. This laser power, corresponding very approximately to a maximum temperature of 500 K, is sufficient to lead to  $\beta$ -elimination in  $\text{Et}_3\text{Ga}$  but not to bring about decomposition of  $\text{Me}_3\text{Ga}$  alone [39].

### FT IR Study of the Pyrolysis Products

Figure 7 shows the FTIR spectrum of a mixture of TMGa (5 torr), TEGa (5 torr) and  $\text{SF}_6$  (10 torr), both before (A) and after (B) extended exposure to 2 W of  $\text{CO}_2$  laser radiation for 300 seconds. In the initial stage of pyrolysis, a viscous condensate formed on the cell walls and this was accompanied by a strong absorption at around  $1650\text{ cm}^{-1}$  in the IR spectrum. This was identified from earlier work [45] as the asymmetric Ga-H-Ga stretch in dimethylgallane. Sharp features due to ethane were also observed at 2989, 1889 and  $949\text{ cm}^{-1}$ . 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  $1182\text{ cm}^{-1}$ . These are assigned to the stable dimeric form of dimethylgallane,  $\text{Me}_2\text{Ga}(\mu\text{-H})_2\text{GaMe}_2$  [30]. 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 a rapid pumping away of ethene and  $\text{SF}_6$ , followed by addition of fresh  $\text{SF}_6$  and further pyrolysis, thus driving the system towards dimethylgallanes and

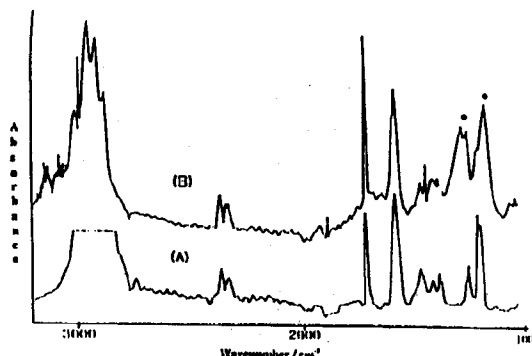


Fig. 7: FTIR spectrum of the products of the IR LPHP of mixture of  $\text{SF}_6$ , TMGa and TEGa before (A) and after (B) exposure of 2 W of laser power for 300 seconds.

monoalkylgallanes. Figure 8 shows the infrared spectrum of DMGaH in the vapour phase after pumping away all volatile materials, notably ethene and  $\text{SF}_6$ . Evidently, in this system  $\beta$ -elimination is reversible; this phenomenon is well known in the corresponding aluminium-based systems, and the ease of insertion of ethene into Ga-H bonds was demonstrated by Pulham *et al.* in their synthesis of  $\text{Et}_2\text{GaH}$  [42].

### $^1\text{H}$ NMR Study of Pyrolysis Products

Following irradiation for approximately 45 minutes at 1.5 to 2.0 W of laser power, the reaction cell was cooled to 77 K and pumped to remove ethene and  $\text{SF}_6$ . The remaining contents of the cell

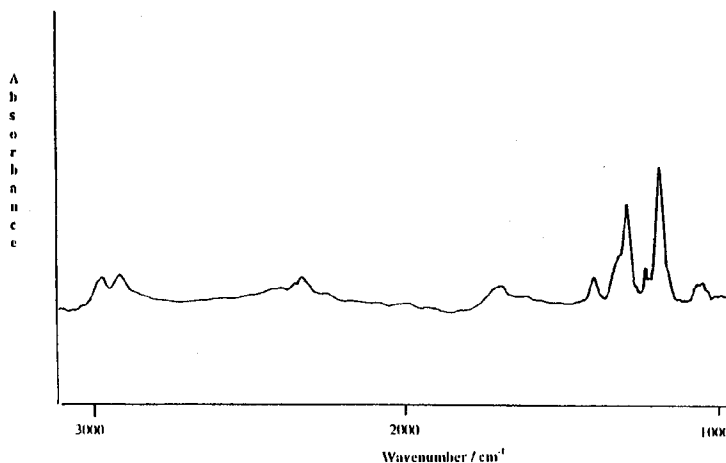


Fig. 8: FTIR spectrum of pure sample of the product of IR LPHP of TMGa and TEGa mixture.

were then rapidly condensed into NMR tube at the same temperature.

The  $^1\text{H}$  NMR spectrum of the pyrolysis cell was rather complex, as can be seen in figure 9(A) which shows the presence of at least five broad Ga-H peaks (between  $\delta_{\text{H}}$  2.70 and 3.00 ppm) at 2.77, 2.79, 2.84, 2.86 and 2.95 ppm at 207 K. The methyl group resonances fall into two sets, a broad singlet at  $\delta_{\text{H}}$  - 0.17 ppm, similar to that observed for the pre-pyrolysis mixture and assigned to the trialkylgallanes, and a complex set between  $\delta_{\text{H}}$  0.00 ppm and  $\delta_{\text{H}}$  0.20 ppm attributed to methyl gallium hydrides, shown in figure 9(B). Similarly, the ethyl  $\text{CH}_2$  resonance appears as an isolated quartet at  $\delta_{\text{H}}$  0.30 ppm arising from trialkylgallane, and a complex overlapped cluster near  $\delta_{\text{H}}$  0.70 ppm arising from ethyl gallium hydrides. The  $\text{CH}_3$  substituent of the ethyl groups yields bands that are overlapped ( $\delta_{\text{H}}$  1.24-1.33 ppm). Simultaneous high power homonuclear decoupling of all hydride resonances resulted in a pronounced sharpening of the Ga- $\text{CH}_3$  and the ethyl  $\text{CH}_2$  features, confirming the origin of these peaks and indicating a  $^3\text{J}(\text{H}-\text{Ga}-\text{C}-\text{H})$  coupling constant smaller than the line width (0.5 Hz). Examination of these patterns revealed at least ten methyl resonances and broad unresolved ethyl  $\text{CH}_2$  peaks. The most intense of the methyl resonances corresponds to dimethylgallane [29] ( $\delta_{\text{H}}$  0.06 ppm) and can be matched to the strong isolated hydride peak at 2.95 ppm. The origin of the rest of the species relies on the fact that dialkylgallanes exist in solution as trimers or larger units,  $\text{R}_{2\text{n}}\text{Ga}_\text{n}\text{H}_\text{n}$ . Exchange of Me and Et group is very rapid, and due to the higher ratio of Me to Et groups, the dominant species will therefore be  $\text{Me}_{2\text{n}}\text{Ga}_\text{n}\text{H}_\text{n}$ , followed by  $\text{Me}_{2\text{n}-1}\text{EtGa}_\text{n}\text{H}_\text{n}$  and  $\text{Me}_{2\text{n}-2}\text{Et}_2\text{Ga}_\text{n}\text{H}_\text{n}$ , with negligible contribution from more highly ethylated species. Figure 10 shows the resulting stereochemical consequence when  $n=3$ . The dominant species (A) exhibits three Me resonances in the ratio 1:2:2 (1) in figure 10. 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. Perhaps the most interesting aspect of the mixed system is the structural information revealed by the spectroscopic observations. From the NMR spectrum of pyrolysis products, it is very evident from figure 10 that several environments are available to Ga-Me groups in the dialkylgallane mixture. The most intense peak, at 0.05 ppm, is easily assigned to  $[\text{Me}_2\text{GaH}]_2$ . The origin of the remainder becomes

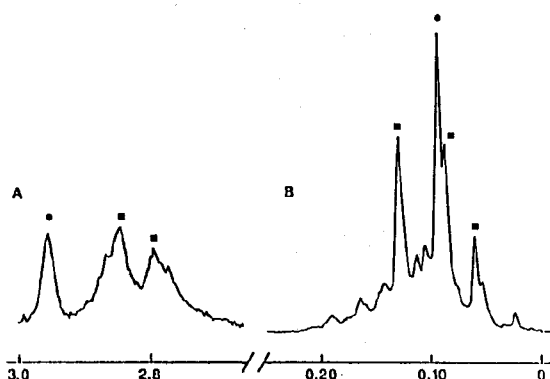


Fig. 9:  $^1\text{H}$ -NMR spectrum of the pyrolysis product of the IR LPHP of TMGa and TEG at 203 K. Only the region of Ga-H (A) and Ga- $\text{CH}_3$  (B) resonances are shown, with features arising from  $\text{Me}_6\text{Ga}_3\text{H}_3$  ( $\otimes$ ) and  $\text{Me}_5\text{EtGa}_3\text{H}_3$  ( $\square$ ) identified.

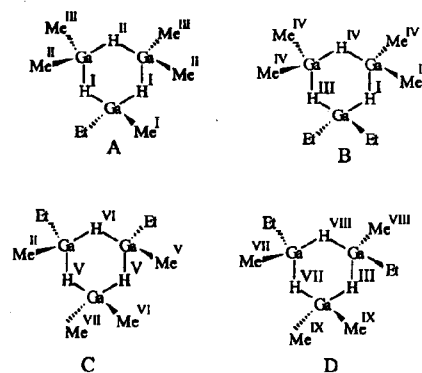


Fig. 10: Ga-Me and Ga-H environments in  $\text{Me}_3\text{EtGa}_3\text{H}_3$  (A) and  $\text{Me}_4\text{Et}_2\text{Ga}_3\text{H}_3$  (B = gem diethyl, C = cis diethyl, and D = trans diethyl). The  $\text{Ga}_3\text{-H}_3$  ring is assumed to be planar in each case.

clear when we consider the nature of the dialkylgallanes in solution, where there is abundant evidence that species such as trimeric or higher units exist, but the dominant species is  $\text{Me}_2\text{GaH}$ .

At room temperature all hydride, methyl and ethyl resonances collapse into single features. Integration of this spectrum provided an estimate of relative Me:hydride:Et proportions of 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  $\delta_{\text{H}}$



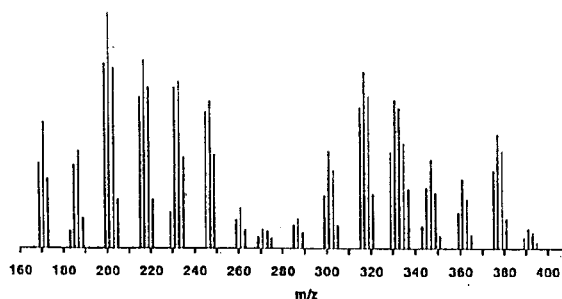


Fig. 11: Mass spectrum ( $m/z$  from 160 to 400) of a solution in  $d^8$ -toluene of a mixture of  $Me_2GaH$  and  $Et_2GaH$ .

4.50 ppm was observed in this spectrum, similar to that produced by the disproportionation of monoethylgallane in the work of triethylgallane [45].

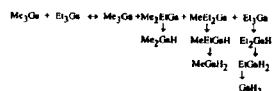
#### Mass Spectra of Pyrolysis Products.

The mass spectrum of organogallanes are known to be complex shown in figure 11, the spectrum is dominated by peaks characteristic of methylgallane system, namely gallium atoms ( $m/z = 69$  and  $71$ ), and  $Me_2Ga^+$  ( $m/z = 99$  and  $71$ ); [46] these features are not shown in figure 4.11. Of more significance here are the two series of clusters which can be attributed to dimeric  $Ga_2$  species (starting near  $m/z = 200$ ) and trimeric species (starting near  $m/z = 300$ ). These can be ascribed to ions arising from the two series  $Me_{4-n}Et_nGa_2H_2$  ( $n = 0 - 4$ ) and  $Me_{6-n}Et_nGa_3H_3$  ( $n = 0 - 6$ ). Each cluster contains peaks arising from the  $Ga_n$  units ( $^{69}Ga_2$ ,  $^{69}Ga$   $^{71}Ga_2$  and  $^{71}Ga_2$  in the ratio 0.36:0.48:0.16;  $^{71}Ga_3$ ,  $^{69}Ga_2$   $^{71}Ga$ ,  $^{69}Ga$   $^{71}Ga_2$ , and  $^{71}Ga_3$  in the ratio 0.22:0.43:0.29:0.06), and is dominated by the ions formed by loss of a proton. Thus, in the cluster near 200, the major peaks arise from  $Me_4Ga_2H^+$  ( $m/z = 199$ , 201 and 203); the most abundant ion in the trimeric cluster near 300 in  $Me_6Ga_3H_2^+$  ( $m/z = 299$ , 301, 303, and 305). Heavier cluster in each series arises from successive replacement of Me by Et; in these, the patterns are more complex, reflecting the well-known additional fragmentation pathways available to methyl-ethyl groups. Cluster below 200 or 300 arise from loss of alkyl groups. Significantly, there are no substantial peaks ascribable to tetrameric or heavier oligomers (the strongest group, near  $m/z = 433$ , is less than 2% of that near 200). We conclude from this that the toluene solution contains significant amounts of dimer and trimers, but no higher

oligomers. This contrasts with the finding of Baxter *et al.*, [30] who showed conclusively that the vapour of  $Me_2GaH$  contains only dimers.

$^{a}Me_2GaH$ (vapour)	$^{b}Me_2GaH$	$^{c}Me_2GaH$	Assignment
2982	2981		
2919	2921		$\nu(C-H)$
2804			
1706	1705		$\nu(Ga-H)_2$ of $(MeGaH)_2$ with $n = 2, 3$
1478			$(CH)_2 + \nu_{sym}(Ga-C)$
1396	1397		$\nu(Ga-H)_2$
1288	1290	1288	$\nu(Ga-H)_2$
	1223	1222	$\nu_{sym}(CH_3)$
1185	1185	1183	$\nu(Ga-H)_2$
1110	1115		$\nu_{sym}(Ga-C)$ or $\nu_{sym}(Ga-C)$
1071	1071		$\nu_{sym}(Ga-C)$
1006			
	965		
	700		
765	769		$\nu(CH_3)$
720	590		
	532		

$^{a}$  = Bridging H atom,  $^{b}$  = From reference [36]  
 $^{c}$  = IR spectral data of  $DMGaH$  synthesis from  $TMGa$  and  $TMAA$  mixture.  
 $^{d}$  = IR spectral data of  $DMGaH$  after eliminating all the volatile materials synthesis from pyrolysis of  $TEGa$  and  $TMGa$  mixture.



Equation (4): Reaction scheme to show the production of the observed products in the pyrolysis mixture of  $TEGa$  and  $TMGa$ .

Abbreviations and Symbols used in the text are listed below

TMAI	trimethyl aluminium (trimethylgallane), $(CH_3)_3Al$
DMAl	deuterated TMAI, $(CD_3)_3Al$
TMGa	trimethyl gallium (trimethylgallane), $(CH_3)_3Ga$
TMin	trimethyl indium $(CH_3)_3In$
TEGa	triethyl gallium (triethylgallane), $Et_3Ga$
DMAIH	dimethyl aluminium hydride (dimethylalane), $(CH_3)_2AlH$
DMGaH	dimethyl gallium hydride (dimethylgallane), $(CH_3)_2GaH$
RMAA	trimethylamine alane, $AlH_3NMe_3$
MOCVD	metal organic chemical vapour deposition
MOVPE	metal organic vapour phase epitaxy
MBE	molecular beam epitaxy

#### Experimental

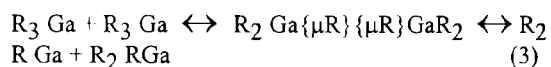
Trimethylgallium and Triethylgallium (high purity grade (99.99 %)) were generously donated by Epichem Ltd. These, and indeed all other compounds employed, notably trimethylamine,  $d_8$ -toluene, and sulphur hexafluoride, were purified by appropriate trap-to-trap distillation and repeated freeze-pump-thaw cycles. All materials were handled on a rigorously pre-conditioned pyrex vacuum line fitted with greaseless Youngs taps. Infrared spectra were recorded using a Digilab FTS40 FTIR spectrometer at  $2\text{ cm}^{-1}$  resolution; all spectra were recorded (either as vapours or as liquid condensed on the windows) using a 10 cm long pyrex cell fitted with ZnSe windows. Although ZnSe does have a rather high cutoff at the low wavenumber end (ca.  $500\text{ cm}^{-1}$ ), for our laser pyrolysis work it has advantages not possessed by other materials.  $^1H$  NMR spectra were recorded at 300.15 MHz using a Bruker AM300 NMR spectrometer while mass spectra were recorded using a Kratos Concept 1H double focussing mass spectrometer (electron impact energy  $\sim 70\text{ eV}$ ).

Samples for NMR and mass spectroscopy were distilled directly from a modified laser pyrolysis cell into sample tubes fitted with Youngs taps, and the  $d_8$ -toluene solvent was added by distillation. All NMR spectra were referenced to the residual  $CD_3$ -protonated solvent at  $\delta_H$  2.10 ppm.

All pyrolysis studies were carried using the method of IR LPHP [47-49]. This technique has been described in detailed in elsewhere [50], and thus only a brief description of the important features are provided here. Pyrolysis was carried out in a pyrex cylinder (length 10 cm, diameter 3.8 cm) fitted with ZnSe windows. The cell was filled with a few torr (1 torr = 133 N m<sup>-2</sup>) of a mixture of the vapour under study and sulphur hexafluoride. The contents of the cell were then exposed to the output of a free-running CO<sub>2</sub> IR laser at power levels of a few Watts. The SF<sub>6</sub> strongly absorbs the laser radiation, which is then very rapidly converted to heat. This produce a strongly inhomogeneous temperature distribution in which the centre of the cell may be heated as high 1500 K, but where the cell walls remains at room temperature. This technique has a number of advantages. The first of these is that pyrolysis is initiated directly in the gas phase, eliminating the complications frequently caused by competing heterogeneous reactions. The second is that primary products of the pyrolysis are rapidly ejected into cool regions of the cell, where they are not directly subjected to further reaction. In favourable cases, these products may be less volatile than the starting materials, and thus accumulated for further investigation. These advantages have already been amply demonstrated in the successful application of the IR LPHP technique to the study of a number of reactions of importance in MOCVD and MOMBE [34].

### Conclusions

The FTIR and NMR observations show clearly that exchange of Me groups with Et or NH<sub>3</sub> occurs rapidly in the gas phase, whereas exchange of Me groups with <sup>1</sup>Bu (or <sup>4</sup>Bu) [17] does not occur. The most likely gas phase mechanism for exchange is metathesis via transient bridge dimers or higher oligomers, for example



Exchange is only thought to be favourable for alkyl groups which have a tendency towards bridge

formation, which in turn is directly related to size in that the exchange rate is in the order Me > Et > <sup>1</sup>Pr > <sup>1</sup>Bu > <sup>4</sup>Bu, and also due to the fact that the corresponding trialkylalanes dimerize; it is therefore expected that trialkylgallane will undergo exchange reactions.

The IR LPHP studies of TMGa + TEGa mixtures are very revealing, both in their own right and in the additional light they shed on the TEGa system. The first conclusion is that at moderate temperatures the products observed are consistent with the almost complete removal of Ga-bound ethyl groups and retention of methyl groups. This confirms the contention that  $\beta$ -elimination is strongly preferred to Ga-R bond homolysis. The products identified are entirely consistent with exchange of alkyl groups, coupled with the loss of Ga-Et groups via  $\beta$ -hydride elimination, the overall chemistry is summarised in equation (4). The laser pyrolysis of TMGa + TEGa has provided a novel route to the production of dialkylgallanes [49], in particular dimethylgallane in previous work [36]. These workers reduced trimethylgallane using sodium tetrahydridogallate, which is itself prepared from gallium(III) chloride and sodium hydride in diethylether at room temperature, to produce dimethylgallane. This was shown to be dimeric in the vapour phase from spectroscopic evidence, and is consistent with our observations.

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 paper 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.

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