

Association and exchange in dialkylgallanes in toluene solution

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Abstract

Solutions of mixtures of dimethylgallane and diethylgallane in toluene were investigated by mass spectrometry and proton NMR spectroscopy. The mass spectrometric observations revealed the presence of dimeric and trimeric species. The NMR data confirmed this conclusion, and further suggested that intramolecular exchange processes are fast even at 200 K, whereas intermolecular exchange is significant only above 250 K.

Keywords: Gallium; Dialkylgallanes; Association; Exchange

1. Introduction

The simple alkyls of gallium and aluminium have recently acquired considerable commercial significance through their potential for metal deposition in processes such as metal organic chemical vapour deposition (MOCVD) [1]. This has sparked a renewed interest in the chemistry of these compounds and their derivatives. We have recently initiated an extensive programme of investigation into the pyrolysis of MOCVD precursors, using the techniques of IR laser-powered homogeneous pyrolysis (IR LPHP) [2]. In particular, we have undertaken a study of the mechanisms of pyrolysis of trimethylgallane [3], triethylgallane [4,5], tripropylgallane [6] and tributylgallanes [7]. In these studies, we have shown that β -hydride elimination is heavily favoured over of radical bond homolysis. In all studies, we have made extensive use of gas-phase IR spectroscopy and ^1H NMR (in toluene- d_8 solution) for the identification and measurement of products. In many instances, this identification has been frustrated because of the complex chemistry of gallane derivatives, which exhibit a wide range of association and exchange phenomena.

We recently reported the results of a study of mixtures of trimethylgallane and triethylgallane [8]. In that

work, we showed that the products of pyrolysis of this model heteroleptic system were a complex mixture of methyl- and ethylgallanes. The ^1H NMR spectrum of the mixture of initial products was complicated by the presence of many isomers, and also by the several possible degrees of association, and convincing identification was possible not at that stage. Fortunately, the formation of adducts with the Lewis base NMe_3 simplified the spectrum considerably. We now report further investigations of the NMR spectra, together with mass spectrometric studies of toluene solutions.

2. Experimental

Trimethylgallane and triethylgallane (high-purity adduct purified grade) were generously provided by Epicchem. These and all other compounds were purified before use by 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 cm^{-1} resolution. ^1H NMR spectra (both one- and two-dimensional) were recorded in toluene- d_8 solution at 300.15 MHz using a Bruker AM300 FT NMR spectrometer. Mass spectra were recorded from toluene solutions using electron impact ionization at 70 eV.

Mixtures of diethylgallane and dimethylgallane were prepared in the gas phase from mixtures of triethylgallane and trimethylgallane using IR LPHP [9,10]. As

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shown previously [8], a judicious choice of the pyrolysis conditions (laser power, duration of irradiation and gas composition) results in complete conversion of trialkylgallanes into dialkylgallanes through partial β -hydride elimination of ethyl groups and retention of methyl groups. The balance of Me and Et groups in the final mixture of dialkylgallanes is determined by that in the initial mixture. The moderately volatile dialkylgallane products were separated from other more volatile components (SF_6 photosensitizer, the ethene β -hydride elimination product and unchanged starting material) by fractional distillation at reduced temperature. Dialkylgallane mixtures produced in this way contained less than 1% of non-gallane impurities as detected by mass spectrometry, and less than 2% of trialkylgallanes as indicated by the ^1H NMR spectra of NMe_3 adducts.

3. Results and discussion

The FTIR spectrum of the products of pyrolysis of a methylgallane-rich initial mixture was reported previously [8]. That spectrum contained peaks characteristic of dimeric Me_2GaH [11], with little evidence of the broad and strong bands ascribed in previous work to Ga–H–Ga bridging vibrations in the higher oligomers of Et_2GaH [4,5,12]. These products, after purification as described above and dissolution in toluene- d_8 , yielded the mass spectrum in Fig. 1 (peaks of 2% or less have been omitted for greater clarity).

The mass spectra of organoalanes and gallanes are known to be complex, and interpretation must be made with care [13]. In the case of the gallanes, the spectrum is dominated by peaks characteristic of methylgallane systems, namely gallium atoms ($m/z = 69$ and 71), and Me_2Ga^+ ($m/z = 99$ and 71) [14]; these features are not shown in Fig. 1. 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 $\text{Me}_{4-n}\text{Et}_n\text{Ga}_2\text{H}_2$ ($n = 0-4$) and $\text{Me}_{6-n}\text{Et}_n\text{Ga}_3\text{H}_3$ ($n = 0-6$). Each cluster con-

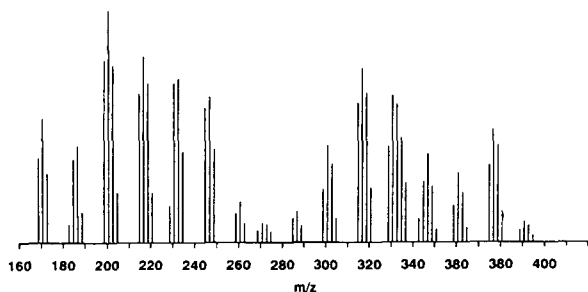


Fig. 1. Mass spectrum (m/z from 160 to 400) of a solution in toluene of a mixture of Me_2GaH and Et_2GaH (Me:Et \approx 2:1).

tains peaks arising from the Ga_n units ($^{69}\text{Ga}_2$, $^{69}\text{Ga}^{71}\text{Ga}$ and $^{71}\text{Ga}_2$ in the ratio 0.36:0.48:0.16; $^{69}\text{Ga}_3$, $^{69}\text{Ga}_2^{71}\text{Ga}$, $^{69}\text{Ga}^{71}\text{Ga}_2$ and $^{71}\text{Ga}_3$ in the ratio 0.22:0.43:0.29:0.06), and is dominated by ions formed by loss of a proton. Thus, in the cluster near $m/z = 200$, the major peaks arise from $\text{Me}_4\text{Ga}_2\text{H}^+$ ($m/z = 199$, 201 and 203); the most abundant ion in the trimeric cluster near $m/z = 300$ is $\text{Me}_6\text{Ga}_3\text{H}_2^+$ ($m/z = 299$, 301, 303 and 305). Heavier clusters in each series arise from successive replacement of Me by Et; in these, the patterns are more complex, reflecting the well known additional fragmentation pathways available to metal-ethyl groups. Clusters below $m/z = 200$ or 300 arise from loss of alkyl groups. Significantly, there are no substantial peaks ascribable to tetrameric or heavier oligomers (the strongest group of peaks, near $m/z = 433$, is less than 2% of that near $m/z = 200$). We conclude that the toluene solution contains significant amounts of dimers and trimers, but no higher oligomers. This contrasts with the findings of Baxter et al. [11], who showed conclusively that the vapour of Me_2GaH contains only dimers.

^1H NMR spectra of toluene- d_8 solutions of a number of dialkylgallane mixtures were recorded over a range of temperatures. At low temperatures, the Ga–H–Ga units give rise to a number of broad overlapped resonances in their characteristic region between δ_{H} 3.00 and 2.60 ppm, the exact shape and number depending on the concentration, the Me:Et ratio and temperature. Although resonances assignable to Me_2GaH and Et_2GaH could be identified, the heavily overlapped nature of these signals made further analysis unprofitable; however, it is significant that these peaks broadened further with increase in temperature, and coalesced above 250 K to yield a single resonance at the composition-weighted mean of those of Me_2GaH and Et_2GaH [3]. Ethyl resonances near δ_{H} 1.30 ppm (Ga– CH_2CH_3) and 0.70 ppm (Ga– CH_2CH_3) behaved similarly, and were also heavily overlapped; however, integration of the Ga– CH_2CH_3 and Ga– CH_3 regions at room temperature could be used to provide a very convenient measure of the Me:Et ratio in the mixture.

The most revealing portion of the spectrum arises from Ga– CH_3 protons, and this region is shown in Fig. 2 for several Et:Me ratios at 200 K. At low temperature, concentration and Et:Me ratio, a number of partially overlapped peaks were discernible; these became more clearly resolved on decoupling of the Ga–H protons (as shown in the lowest trace of Fig. 2), confirming that these resonances do indeed originate from Me groups in molecules containing Ga–H units, and that H–Ga– CH_3 coupling does make some contribution to the linewidth. The central and upper traces in Fig. 2 are spectra of mixtures containing increasing Et:Me ratios, recorded without Ga–H decoupling; the upper spectrum is that of a considerably more concentrated solution.

The marked intensity shift in favour of higher field resonances is strongly suggestive of an increasing number of Et groups in these species. Proton–proton correlation spectroscopy revealed that the strong peak at lowest field (marked A in trace 1) was not correlated with any ethyl group resonances, whereas all other peaks were; as indicated by the decoupling experiments, all resonances were correlated with Ga–H resonances. As the temperature was raised, all resonances broadened and coalesced; in mixtures containing traces of unreacted Me_3Ga , the single peak arising from this species was also evidently involved in rapid exchange.

These spectra are clearly very complex, reflecting the large number of species present in solution. However, they can be accounted for almost quantitatively in terms of the following simple model. We assume that the solution contains both dimeric species and trimeric species, with the former dominant, as indicated by the mass spectrum. We further assume that the relative concentrations of species within each series (i.e. $\text{Me}_{4-n}\text{Et}_n\text{Ga}_2\text{H}_2$ and $\text{Me}_{6-n}\text{Et}_n\text{Ga}_3\text{H}_3$) are statistically determined by the overall Me:Et ratio. The observation of distinct peaks for members of these series suggests that intermolecular exchange processes (which would require extensive dissociation and reassociation of Ga–H bonds) are slow at the temperature of the spectra; on the other hand, intramolecular exchange of alkyl groups within each member of the series is relatively rapid, since it does not require breaking of more than one Ga–H–Ga bond. If we now consider a given Me group in the dimeric complex $\text{Me}_3\text{EtGa}_2\text{H}_2$, for example, we find that its mean environment may be represented by $\text{Me–GaH}_2\text{Et}_{0.33}\text{Me}_{0.67}$; similarly, that in the trimeric

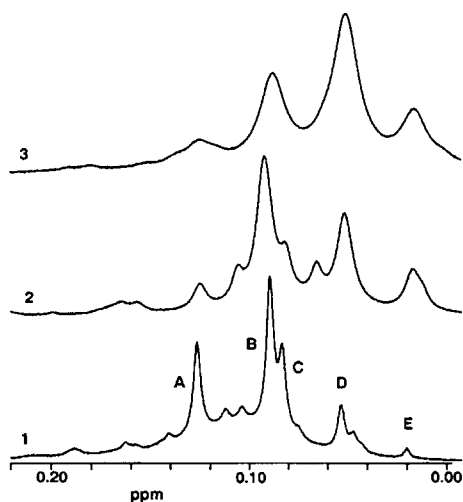


Fig. 2. ^1H NMR spectra (δ_{H} from 0.22 to 0.00) of mixtures of Me_2GaH and Et_2GaH in toluene at 200 K. (1) Me:Et \approx 6:1, Ga–H protons decoupled; (2) Me:Et \approx 1.2:1, no decoupling; (3) Me:Et \approx 1:2, no decoupling. The ratios of the concentrations in traces 1, 2 and 3 are approximately 1:2:4. See text for further discussion.

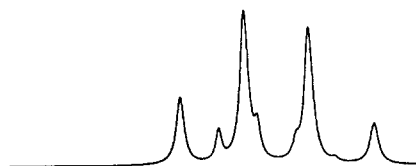


Fig. 3. ^1H NMR spectrum of Me protons in a $\text{Me}_2\text{GaH} + \text{Et}_2\text{GaH}$ mixture simulated according to the model described in the text. Parameters were chosen to match the spectrum of Fig. 2, trace 2, as closely as possible; Me:Et ratio = 1.2:1, dimer:trimer ratio = 2.5:1.

$\text{Me}_4\text{Et}_2\text{Ga}_3\text{H}_3$ would be $\text{Me–GaH}_2\text{Et}_{0.4}\text{Me}_{0.6}$. Our observations of the series of four-coordinated species $\text{Me}_{3-n}\text{GaEt}_n \cdot \text{NMe}_3$ and $\text{Me}_{2-n}\text{GaEt}_n\text{H} \cdot \text{NMe}_3$ showed that successive replacement of Me groups by Et groups results in a constant incremental upfield shift in the Me–Ga ^1H NMR resonance [8], and it is reasonable to expect that the same trend will be observed in the present systems. We therefore assign the four approximately equally spaced strong peaks marked A, B, D and E in trace 1 to the series $\text{Me}_4\text{Ga}_2\text{H}_2$, $\text{Me}_3\text{EtGa}_2\text{H}_2$, $\text{Me}_2\text{Et}_2\text{Ga}_2\text{H}_2$ and $\text{MeEt}_3\text{Ga}_2\text{H}_2$, consistent with the intensity, correlation and expected chemical shifts in these species. The majority of the weaker signals may be attributed to a similar trend in the less abundant trimeric series, with the peak marked C corresponding to the most predominant member $\text{Me}_4\text{Et}_2\text{Ga}_3\text{H}_3$. Fig. 3 is a spectrum based on this model with parameters chosen to fit most closely the conditions of Fig. 2, trace 2; although not perfect, the match of the major features is sufficiently close to lend support to the model we proposed.

In conclusion, the mass spectrometric evidence strongly suggests that dialkylgallanes $\text{RR}'\text{GaH}$ exist as H-bridged dimers and trimers in toluene solution, and that exchange processes lead to a statistical distribution of all possible forms. The NMR studies support this view, and further indicate that intramolecular exchange of alkyl groups is rapid even at 200 K, but that intermolecular redistribution does not become significant until 250 K.

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