

Infrared Laser Powered Pyrolysis of Triethylgallane: First Evidence for a Free Monoalkylgallane

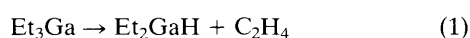
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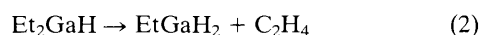
Ethylgallane, characterised by the IR and ^1H NMR spectra of its trimethylamine adduct, has been identified as an intermediate in the infrared laser powered pyrolysis of triethylgallane, providing the first unambiguous evidence for the existence of free monoalkylgallanes.

Until recently, the chemistry of gallium hydrides was largely restricted to complexes in which the GaH_n ($n = 1-3$) unit was stabilised through coordination to Lewis bases such as NMe_3 .¹ Unambiguous reports of free gallanes were limited to the dialkylgallanes $(\text{R}_2\text{GaH})_n$, where $\text{R} = \text{Me}$,² Et ,³ or Bu ,⁴ and $n = 2$ or 3 . There have been no reports of free monoalkylgallanes, $(\text{R}\text{GaH}_2)_n$, although NMR and IR evidence for adducts such as $\text{MeGaH}_2\cdot\text{NMe}_3$ has been presented.⁵ In the past few years, however, a number of novel routes to gallanes have been reported, including the elusive parent Ga_2H_6 .⁶

We recently reported the synthesis of diethylgallane, Et_2GaH , in the infrared laser powered homogeneous pyrolysis (IR LPHP) of triethylgallane *via* the β -elimination reaction,⁷ eqn. (1).



In the present Communication, we report observations of the prolonged IR LPHP of Et_3Ga , and we present conclusive evidence for the production of free (*i.e.* uncomplexed) monoethylgallane in a second β -elimination step, eqn. (2). These observations represent the first reported evidence for the existence of a free monoalkylgallane.



The technique of IR LPHP is described in detail elsewhere.^{8,9} Briefly, a mixture of triethylgallane and SF_6 (as an IR absorber and energy transfer agent) at pressures of a few Torr (1 Torr = 133 N m^{-2}) is contained in a Pyrex cell of volume 50 cm^3 , fitted with ZnSe windows. The gas mixture is exposed to the output of a free-running CO_2 laser, and the cell contents are monitored using FTIR spectroscopy. As shown elsewhere,^{8,10} this arrangement generates a highly non-uniform temperature profile in which the temperature at the centre of the cell may be as high as 1500 K , but in which the cell walls remain at room temperature. The advantages of this system arise from the use of very small quantities of material and an enhancement of the lifetime of unstable products; this latter point is a consequence of the rapid migration of primary products into cool regions of the cell on formation. In particular, involatile products are condensed onto the cold cell walls, where they are not subject to further pyrolysis.

The FTIR spectra of a mixture of Et_3Ga (4 Torr) and SF_6 (10 Torr) before and after brief (30 s) laser irradiation were presented in an earlier Communication.⁷ Subsequent investigation has shown that features identified therein as Et_2GaH arise largely from the liquid phase product; this was demonstrated by distillation from cell wall to window and *vice versa*. On further pyrolysis, the FTIR spectrum indicated the presence of a greater quantity of ethene, and additional changes in the region of the very strong Ga-H stretching absorption around 1640 cm^{-1} . The details of these changes were, however, obscured by the considerable width of this feature. On rapidly pumping away the relatively volatile C_2H_4 product and SF_6 photosensitiser and condensing the remaining liquid product into carefully dried $\text{C}_6\text{D}_5\text{CD}_3$, a ^1H NMR spectrum of what appeared to be pure Et_2GaH (*i.e.* free from

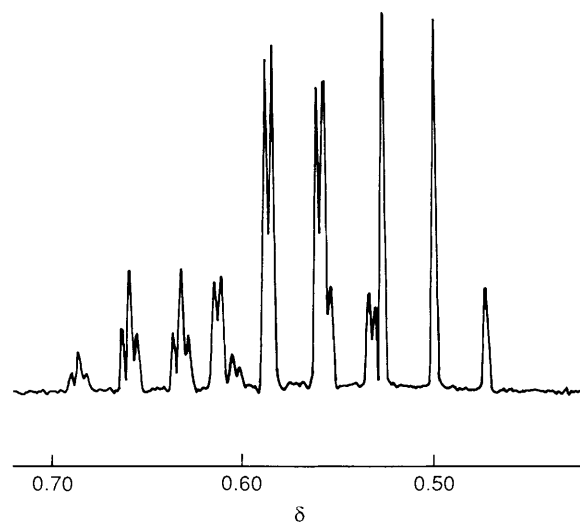


Fig. 1 ^1H NMR spectrum (300 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, -60°C , referenced to TMS) of NMe_3 adduct of products of prolonged IR LPHP of Et_3Ga . Only the region of CH_2 resonances is shown: singlets arise from $\text{Et}_3\text{Ga}\cdot\text{NMe}_3$, doublets from $\text{Et}_2\text{GaH}\cdot\text{NMe}_3$ and triplets from $\text{EtGaH}_2\cdot\text{NMe}_3$.

Et₃Ga) could be observed.⁷ By varying the period of pyrolysis, small deviations from a 1:6 ratio in the GaH:CH₃ signals identified earlier were observed, but these were not conclusive. At higher laser powers (*i.e.* temperatures), other hydrocarbon products were observed, presumably arising from the competing bond homolysis pathway.

However, incontrovertible evidence for the presence of EtGaH₂ in the liquid product of prolonged pyrolysis was obtained on addition of carefully distilled NMe₃, which forms well-documented adducts with gallanes.^{1,5,11} The FTIR spectra thus produced revealed two sets of peaks that clearly belonged to different products. In particular, two intense peaks in the Ga–H stretching region at 1798 and 1820 cm⁻¹, which correlate in intensity with two equally strong peaks in the H–Ga< bending region at 820 and 752 cm⁻¹ respectively, were observed. The first of these in each case may be identified as arising from the adduct Et₂GaH·NMe₃, whereas the second arise from the adduct EtGaH₂·NMe₃. Although neither species has been previously reported, this identification is confirmed by analogy with the corresponding methyl adducts^{5,11} and by our FTIR studies of exchange reactions in mixtures of GaEt₃ and AlH₃·NMe₃, reported elsewhere.¹² The clearest evidence, however, comes from the ¹H NMR spectrum of the adduct mixture in C₆D₅CD₃ at –60 °C. This includes two singlets at δ_H 5.00 and 5.09 with the broadness typical of protons attached to Ga. The region associated with the CH₂ protons (δ_H 0.40 to 0.70) is particularly informative, and is illustrated in Fig. 1. In addition to a quartet splitting arising from coupling to Me protons (*J*_{HH} 8.0 Hz), the forms EtGaH₂·NMe₃ and Et₂GaH·NMe₃ exhibit respectively a triplet and doublet splitting (*J*_{HH} 1.1 Hz) arising from GaH protons. This spectrum is of some significance, since it represents the first observation of a ³J coupling arising from a proton directly attached to Ga. On warming to room temperature, the two GaH resonances collapse into a broad singlet, and splittings of the CH₂ resonances by the GaH protons disappear. These observations are readily attributed exchange of GaH protons between these forms in solution. However, the Et groups do not appear to be subject to exchange at this temperature. Evidently, the formation of the NMe₃ adduct slows exchange considerably, since no evidence of coupling to the Ga–H proton in Et₂GaH was observed, even at –70 °C.⁷ In some cases, there was also some Et₃Ga·NMe₃ present, arising either from unreacted Et₃Ga or from disproportionation reactions.³ The integrated ratio of these three species is entirely in accord with our assignment of the FTIR spectra, and with the length of exposure to IR LPHP.

We attribute these observations to successive β-elimination steps [eqn. (1) and (2)] in the IR LPHP of Et₃Ga. An

alternative hypothesis is that disproportionation of Et₂GaH yields EtGaH₂ after NMe₃ adduct formation. However, this can be discounted in the gas phase, since it is possible to remove selectively any EtGaH₂·NMe₃ by further mild IR LPHP without altering the amount of Et₂GaH·NMe₃ present. Under some circumstances, this leads to the observation of GaH₃·NMe₃, also identified in our exchange studies of both Et₃Ga + AlH₃·NMe₃¹² and Me₃Ga + AlH₃·NMe₃¹³ mixtures. However, it cannot definitely be ruled out that there is an equilibrium between Et₂GaH and EtGaH₂ in the liquid product of IR LPHP, with the position of equilibrium determined by the partial pressure of Et₃Ga remaining. However, we may conclude with some confidence that this liquid product is an oligomeric or polymeric form composed of formal Et₂GaH and EtGaH₂ units in a ratio determined by the length of time of pyrolysis; it is of structural significance that no vibrations corresponding to non-bridging Ga–H bonds are observed in the FTIR spectrum of the liquid. The failure to observe unambiguous NMR signals due to native EtGaH₂ probably arises from its low volatility.

We thank the SERC for a studentship to A. S. G. and a fellowship to R. D. M., and for grants towards the purchase of equipment. We also thank Dr A. C. Jones, of Epichem Ltd, for the donation of chemicals and for helpful discussions.

Received, 3rd October 1990; Com 0104472E

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