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MOVPE Mechanisms from studies of specially designed and labelled precursors

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Studies of the reaction or decomposition products of precursors for metal organic vapour phase epitaxy (MOVPE) do not always give enough information to allow the unequivocal determination of decomposition or growth mechanisms. By studying deuterium labelled precursors in the presence or absence of their protio analogues, other precursors and/or He, H_2, D_2 or by studying precursors carrying substituents that are designed to give different products if different mechanisms operate, it is possible to draw more definitive conclusions.

Using these studies coupled with semi-empirical molecular orbital calculations, it is shown that primary arsines decompose by reductive elimination of H_2 followed by β-abstraction (Bu^tAsH_2) or reaction with the parent arsine to form RAsH·, which undergoes reductive elimination (PhAsH·), β-abstraction ($Bu^tAsH·$) or As–C bond cleavage ($Bu^tAsH·$). Hex-5-enylarsine has been used to show that adduct formation is not important during growth of GaAs.

For group 16 dialkyls (R_2E, E = S, Se or Te), the predominant decomposition mechanism is homolytic E–C bond cleavage. Subsequent reactions involve abstraction of H from the β-position of the intact R_2E to give alkane, two molecules of alkene E and H· (E = Te or Se). For E = Te, H· does not react significantly with $Pr^i{}_2Te$, but for $Bu^t{}_2Se$ a short chain-reaction is initiated by H·. The importance of free radicals is confirmed by studies of (but-2-enyl)$_2$Te, (hex-5-enyl)$_2$E (E = S, Se, Te), (pent-5-enyl)$_2$Te and (hex-5-enyl)SH, as well as of secondary and tertiary analogues. Reactions of the labelled and designed group 16 precursors with Me_2M (M = Cd or Zn) are also discussed.

Introduction

Semiconductors are the major components of the computer age. Elemental semiconductors such as silicon from Group 14 have found use in applications from transistors and computers through to solar energy converters, but they have the limitation that the band-gap is fixed so that the wavelengths they can absorb or emit cannot be varied over a wide range. Compound semiconductors, which are made up from elements of Groups 13 and 15, 12 and 16 or sometimes 13 and 16, on the other hand, have a variety of different band gaps which cover the whole electromagnetic spectrum from the IR (InSb) through to the UV (ZnS).[1] Using three or four of these elements, *e.g.* $Cd_xHg_{1-x}Te$ or $Ga_xIn_{1-x}As_yP_{1-y}$, the band gap within one materials system can be varied over a wide range. In addition, the mobility of electrons within some of these materials can be an order of magnitude higher than in silicon.

David Cole-Hamilton received his training in Organometallic Chemistry with Dr T. A. Stephenson (Edinburgh) and Professor Sir Geoffrey Wilkinson (Imperial College). He was on the staff at Liverpool, where Professor A. K. Holliday introduced him to Dr J. B. Mullin (MOD) and the design of MOVPE precursors, before taking up the Irvine Chair of Chemistry in St. Andrews. His work is in the area of organometallic compounds applied to homogeneous catalysis and problems in Materials Chemistry. Some of his work on the production of highly purified metal alkyls has been commercialised through Epichem Ltd (Founded 1983). He was the first Sir Edward Frankland Fellow of the RSC (1984–5) and won the Corday Morgan medal and prize in 1983. In 1998 he won the RSC Industrial award for Organometallic Chemistry sponsored by Monsanto.

For the elemental semiconductors, large single crystals can be grown and cleaved to make the required electronic devices, but the growth of large single crystals of the compound materials has proved highly problematical. Since only a thin film of the semiconductor is usually required for the fabrication of devices, the most important methods to have been developed to surmount this problem involve the growth of thin layers of the desired semiconductor on a single crystal of another, using the ordered array of the substrate atoms to align those of the growing layer. A variety of methods has been devised for doing this, but one of the most important is metal organic vapour phase epitaxy (MOVPE).[1,2] In this approach, highly purified volatile compounds of the elements to be incorporated into the semiconductor are passed over the heated substrate where they decompose to give the thin film. The composition of the growing layer can be controlled by regulation of the gas phase composition and dopants can be included by incorporating extra precursor streams. The technique has proved highly versatile and is now production technology for a variety of semiconductor devices, many of which contain up to 100 layers of different but controlled composition.[2]

The earliest examples of semiconductor growth by MOVPE involved metal alkyls (usually MMe_n) for the Group 12 or 13 precursors and hydrides (EH_n) for the Group 15 or 16 elements.[3,4] In most cases these systems worked well and in some they continue to be used in production.[1] These compounds are, however, highly reactive and often toxic materials[5] so there have been developments in recent years particularly towards the use of different precursors for the Group 15 and 16 precursors. Most of these involve the replacement of the hydrides by compounds that contain one or more alkyl or amide groups and hence the chemistry leading to the semiconductor film becomes more complex and has the potential to incorporate extraneous elements into the growing layer such as carbon or nitrogen, which have detrimental effects on the electronic properties.[6] There is thus a considerable interest in understanding the processes that occur during the growth of layers from these precursors so as to be able to improve on their design.

Various groups have used surface science techniques to study the species present on the surface during growth,[7,8] but often these studies have been carried out under high vacuum and there can be no certainty that the interesting results obtained correlate with what occurs under growth conditions (generally *ca.* 1 atm).

Furthermore, in addition to reactions on the surface, gas phase processes may be occurring of which surface techniques remain ignorant. Gas phase reactions may also determine the nature of the surface species. Kinetic studies have been carried out under real growth conditions and certain conclusions have been drawn on the basis of product analyses (usually using mass spectrometry, gas chromatography–mass spectrometry (GCMS)[9] or FTIR[10] studies). These have given valuable insight, although without quantitative calibration, they are of limited value and, as will be demonstrated, they do not always lead to the appropriate conclusions.

Our approach has been to design precursors which are as similar as possible to those that are used in the growth process, but which, as a result of the products they form, give definitive information about the way in which they decomposed or reacted. We have used two main approaches. The first involves the use of deuterium labelling whilst the second involves the design of special 'reporter ligands', whose reaction products give information on the mechanisms involved in their formation. Product analyses are carried out using multinuclear NMR spectroscopy or GCMS and in some cases these experimental studies are backed up by theoretical calculations. In this article, we discuss our work on gallium arsenide and on II–VI (12–16) semiconductors involving Zn, Cd, Hg, S, Se or Te.

Gallium arsenide

Gallium arsenide was originally grown from $\mathrm{Me_3Ga}$ and $\mathrm{AsH_3}$[3] and some commercial processes still use these precursors extensively.[2] However, $\mathrm{AsH_3}$ is a highly toxic gas and is usually supplied in high pressure cylinders diluted with hydrogen. The risks associated with the possible rupture of one of these cylinders or their ancilliary equipment, either in use or during transport, led to a search for alternative arsenic precursors. The main ones to be introduced were the primary arsines, $\mathrm{Bu^tAsH_2}$ and $\mathrm{PhAsH_2}$, of which $\mathrm{Bu^tAsH_2}$ is now the precursor of choice. These compounds are not intrinsically very much less toxic than $\mathrm{AsH_3}$,[5] but being liquids, they are generally supplied in small metal containers and a spillage is not catastrophic—it simply requires evacuation of the area until the arsenic compound has evaporated and dissipated.

The various first steps in the decomposition mechanisms for $\mathrm{Bu^tAsH_2}$ are shown in Fig. 1. They are, reductive elimination of $\mathrm{Bu^tH}$ or $\mathrm{H_2}$, β-H abstraction to give $\mathrm{AsH_3}$ and 2-methylpropane or homolytic cleavage of the As–C or As–H bond. At the time when we started to work in this area, some elegant studies had been performed that showed that both 2-methylpropene and 2-methylpropane were products.[11,12] All of these only considered that mechanisms that involved loss of the As–C bond, by reductive elimination of 2-methylpropane, by homolytic fission of the As–C bond or by β-H abstraction, were likely to be important since literature values of the bond enthalpies are much higher for As–H than for As–C.[13]

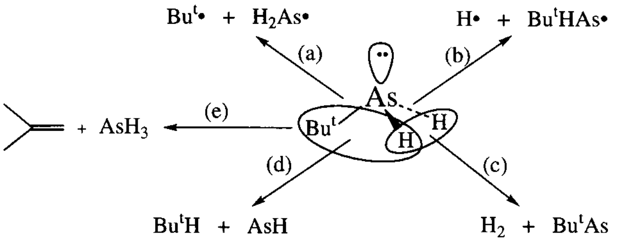

Fig. 1 Possible first steps in the decomposition of $\mathrm{Bu^tAsH_2}$. (a) As–C bond cleavage; (b) As–H bond cleavage; (c) reductive elimination of $\mathrm{H_2}$; (d) reductive elimination of $\mathrm{Bu^tH}$; (e) β-elimination.

We opted to study[13–15] $\mathrm{PhAsH_2}$ since one of the pathways (β-H abstraction) is not available. The organic product from its decomposition is benzene and this could arise from As–C bond cleavage or from reductive elimination. To test which of these was operative, we studied the decomposition of (*o*-tolyl)$\mathrm{AsD_2}$, reasoning that reductive elimination would only give toluene deuteriated in the *ortho* position, whereas homolytic fission would give the *o*-tolyl radical which would either abstract D to give toluene deuteriated in the *ortho*-position or would isomerise to the allylic stabilised benzyl radical which would abstract D to give toluene deuteriated in the methyl group.

Decomposition of *o*-tolyl$\mathrm{AsD_2}$ produced toluene with D in the *ortho*-position, but also in the methyl group. Surprisingly, however, we observed that the methyl group contained 0, 1, 2 or 3 D atoms. This could not easily be explained by any of the mechanisms that had previously been suggested so we carried out calculations in the PM3 system on the various possible first steps in the decomposition, including those which involved As–H bond cleavage. These showed that, at the temperatures involved, loss of $\mathrm{H_2}$ was both kinetically and thermodynamically the most favoured option.[15] We also showed that reductive elimination of toluene from (*o*-toly)AsH· had a very similar free energy of activation to tautomerism to give the stabilised benzyl radical, $\mathrm{H_2AsC_6CH_2\cdot}$; a pathway that could account for multiple D incorporation into the methyl group. This led us to propose that the decomposition of (*o*-tolyl)$\mathrm{AsH_2}$ occurred as shown in Fig. 2, with (*o*-tolyl)As reacting with (*o*-tolyl)$\mathrm{AsH_2}$ to give (*o*-tolyl)AsH· from which the final products were generated. Calculations suggested that a very similar sequence of reactions accounted for the decomposition of $\mathrm{Bu^tAsH_2}$ except that β-H abstraction in $\mathrm{Bu^tAs}$, formed by loss of $\mathrm{H_2}$, competed with the bimolecular reaction to produce $\mathrm{Bu^tAsH\cdot}$.[15]

One of the other controversies surrounding the growth of GaAs by MOVPE concerned whether or not adducts of the form $[\mathrm{Me_3Ga{\cdot}AsR_3}]$ (R = H, alkyl or aryl) were involved in the growth process. There is no doubt that these form at room temperature and below, but at 600–700 °C entropy may ensure that their existence is at best fleeting. We probed this by studying the model primary alkyl arsine, (hex-5-enyl)-$\mathrm{AsH_2}$.[15–18] We selected the hex-5-enyl group originally as a

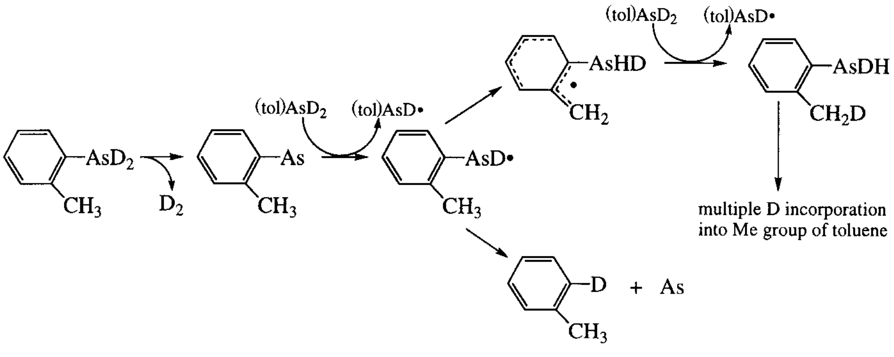

Fig. 2 Proposed mechanism for the decomposition of (*o*-tolyl)$\mathrm{AsD_2}$.

probe for the decomposition mechanism of primary arsines since, if hex-5-enyl radicals are formed at any stage by As–C cleavage, they will cyclise to cyclopentylmethyl or cyclohexyl radicals.[19,20] Non-radical processes will, on the other hand, give straight chain products. The decomposition of (hex-5-enyl)-AsH_2 on its own produces hex-1-ene as the major hydrocarbon product,[16,17] showing that free alkyl radicals are not produced, as confirmed by the decomposition of (*o*-tolyl)AsD_2 and the calculations on Bu^tAsH_2 (see above). When (hex-5-enyl)arsine was reacted with Me_3Ga in the liquid phase at low temperature, we were able to identify the adduct, $[Me_3Ga{\cdot}As(hex)H_2]$ which decomposed on heating, giving off methane, to produce $[Me_2GaAs(hex)H]_3$ then $[MeGaAs(hex)]_n$. Heating the polymer produced GaAs together with methane and methylene-cyclopentene. The last product shows that the final step involves As–C and Ga–C bond cleavage to give Me· and hex-5-enyl radicals, which cyclise to cyclopentylmethyl radicals and react with Me· to give the observed products (see Fig. 3). The different products obtained from the decomposition of [(hex-5-enyl)AsH_2] in the presence or absence of Me_3Ga allow us to determine whether the gas phase reaction involved adduct formation or not, by analysing the products from the gas-phase reaction of Me_3Ga with [(hex-5-enyl)AsH_2]. In practice, we obtained[16,17] a product distribution that is extremely similar to that obtained from [(hex-5-enyl)AsH_2] alone along with methane and unreacted Me_3Ga, confirming that adduct formation is not significant in the gas-phase—at least in this system.

II–VI Compounds

$Cd_xHg_{1-x}Te$, ZnSe, ZnS

Cadmium mercury telluride is the main semiconductor used for IR detectors and emitters. It is also of importance for long range transmission over fibre optic cables made from fluoride glasses. Hydrogen telluride is not sufficiently stable for use in MOVPE[4] so dialkyl- or diallyl-tellurium compounds have generally been employed together with Me_2Cd and elemental mercury.

Diallyltellurium [bis(prop-2-enyl)tellurium] decomposes to give hexa-1,5-diene and tellurium.[21] These products could be produced by reductive elimination or by Te–C bond cleavage to give prop-2-enyl radicals which combine to give the observed product. In order to test which of these mechanisms is operating, we studied[22] the decomposition of [bis(but-2-enyl)tellurium] since reductive elimination should give only octa-2,6-diene (as *Z,Z*, *E,Z* and *Z,E* isomers) whilst formation of butenyl radicals followed by radical coupling should give these products together with 2,4-dimethylhexa-1,5-diene and *Z*- and *E*-3-methylhepta-1,5-diene. In practice, we observed that all the products were observed (Fig. 4) in similar ratios to those obtained from bis(but-2-enyl)zinc, which is known to decompose by a free radical mechanism.[23] Furthermore, at partial conversion there was no evidence for isomerisation of the starting material to bis(1-methylpropenyl)tellurium, ruling out the reductive elimination mechanism.

The main tellurium precursors that have been employed are dialkyltelluriums, especially Pr^i_2Te. To probe the decomposition mechanisms of this kind of alkyl in the presence or absence of Me_2Cd and/or Hg, we have studied the decomposition of bis(hex-5-enyl)tellurium,[24,25] bis(pent-4-enyl)tellurium[24] and of Pr^i_2Te labelled with deuterium.[26]

The model studies in the gas phase showed that a mixture of straight chain and cyclic products was obtained from bis(hex-5-enyl)tellurium indicating that Te–C bond cleavage was certainly important (Fig. 5), but not giving detailed information about subsequent steps in the decomposition. In the liquid phase, bis(hex-5-enyl)tellurium produced linear and cyclic hydrocarbons, but also (cyclopentylmethyl)(hex-5-enyl)tellurium and bis(cyclopentylmethyl)tellurium. Both of these products suggest that the dialkyltellurium undergoes homolytic fission of the Te–C bond and that the free carbon based radical (after cyclisation in this case) reacts back with intact bis(hex-5-enyl)tellurium, eliminating a further hex-5-enyl radical.[24,25] Using bis(pent-5-enyl)tellurium in the liquid or gas phase, we obtain pent-1-ene and penta-1,4-diene together with 2-methyltelluracyclopentane. The last product shows that once Te–C bond cleavage has occurred, the RTe· formed in this case is sufficiently stable to undergo internal cyclisation to the telluracyclopentylmethyl radical which then picks up H·.

These reactions clearly show that Te–C bond cleavage is important, but they involve primary alkyls which differ from those generally employed in growth. We, therefore, studied d^{14}-

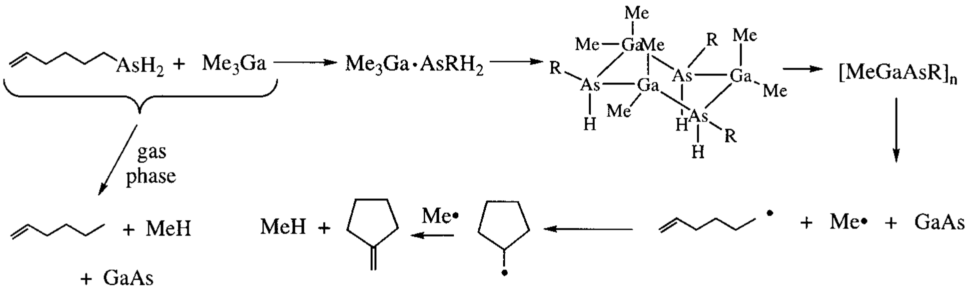

Fig. 3 Reactions occurring during the codecomposition of Me_3Ga with (hex-5-enyl)AsH_2 in the liquid or gas phases (R = hex-5-enyl).

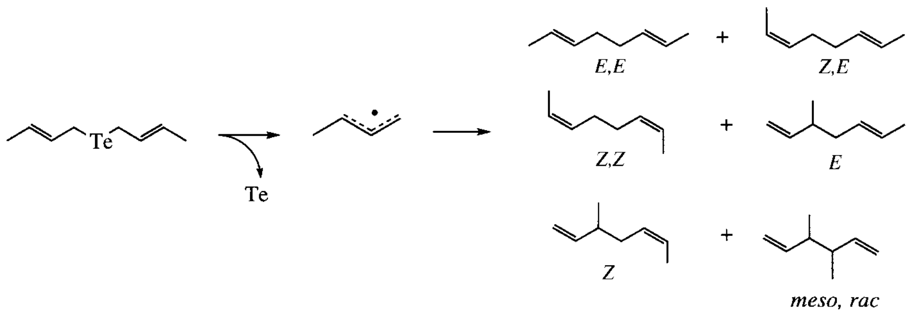

Fig. 4 Proposed mechanism of decomposition of (prop-2-enyl)$_2$Te.

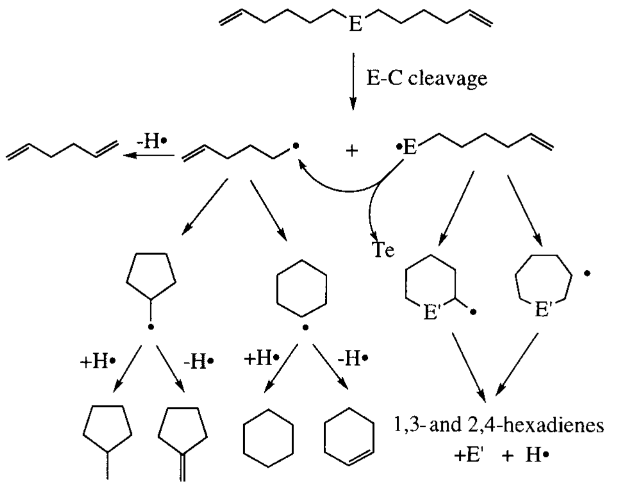

Fig. 5 Proposed mechanism of decomposition of (hex-5-enyl)$_2$E (E = S, Se or Te; E′ = S or Se).

labelled Pr^i_2Te to investigate the pathways open to a real precursor.[26] The organic products from decomposition of unlabelled Pr^i_2Te are propene and propane (2 : 1) together with small amounts of 2,3-dimethylbutane, much less than would be expected from gas phase reactions of $Pr^i\cdot$ with one another.[27] The various possible processes for decomposition of a compound of this type are similar to those shown in Fig. 1 but involve reductive elimination to give 2,3-dimethylbutane, β-H abstraction or Te–C bond cleavage.

Codecomposition of d^0- and d^{14}-Pr^i_2Te gives a mixture of d^0, d^1, d^7 and d^8 propane (1.7 : 1 : 1.5 : 1) together with d^0 and d^6-propene. This strongly suggests that Te–C bond cleavage occurs rather than β-H abstraction followed by competing β-H abstraction and reductive elimination, which might be expected to give only d^0- and d^8-propane together with d^0- and d^6-propene. Care must be exercised here, however, since exchange of [C_3H_7TeH] with [C_3D_7TeD] is expected to occur to give [C_3H_7TeD] and [C_3D_7TeH] from which reductive elimination would give d^1- and d^7-propane. Careful analysis of the product ratios does allow us to distinguish between the two pathways, however, since it can be shown that the expected ratio for the β-H elimination-scrambling-reduction elimination process should be approximately 1 : 1 : 1 : 1 for d^0, d^1, d^7 and d^8-propane (given the *ca.* 1 : 1 ratio of $C_3H_7 : C_3D_7$ observed in the products) whereas kinetic isotope effects should make d^0 and d^7 the major products from a free radical process, as is observed. The fact that the $d^0 : d^1$ ratio (1.7) is very similar to $d^7 : d^8$ (1.5) is consistent with a free radical mechanism with k_H/k_D for H abstraction being *ca.* 1.6. Further support for the free radical processes arises from the fact that we have trapped free alkyl radicals and observed them by EPR spectroscopy during the liquid phase decomposition of simple tellurium alkyls such as Pr^i_2Te.[28,29]

For Pr^i_2Te, carrying out the decomposition in hydrogen increases the amount of propane relative to propene formed and decomposition of d^{14}-Pr^i_2Te in hydrogen produces some C_3D_7H ($d^7 : d^8 \approx 1 : 1$) confirming that $Pr^i\cdot$ is formed and reacts with H_2. To explain the 2 : 1 ratio of propane : propene obtained in the decomposition of Pr^i_2Te in helium, we have proposed that $Pr^i\cdot$ formed from homolytic fission of the Te–C bond abstracts H· from intact Pr^i_2Te initiating a 'cascade' reaction that leads to 2-methylpropane, 2 × 2-methylpropene, Te and H· (Fig. 6).

Recently we have obtained further support for mechanisms of this kind from studies of Bu^tSe,[30–32] a precursor that has recently found favour because H_2Se leads to severe problems associated with prereactions if used with R_2M (R = Me or Et, M = Zn or Cd) to grow MSe,[33] as well as to passivation of N dopants, probably as N–H.[34] We have shown that the prereactions involve cluster growth in the gas phase leading to nucleation as nanoparticles[35–37] and have developed this chemistry into a method for synthesising polymer–nanoparticle composites of these important materials.[38–40] The replacement of H_2E (E = S or Se) by Bu^tEH has been partially successful in eliminating the prereaction,[41,42] although we have recently shown that a different prereaction occurs to give $[Bu^tEMR]_5$ which, in turn decompose on heating to give nanoparticles of ME.[43]

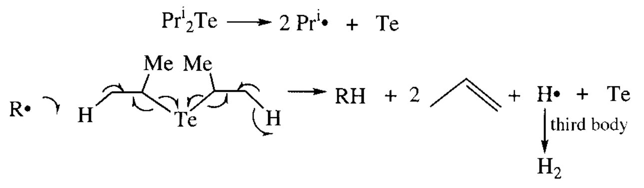

Fig. 6 Proposed major pathway for the decomposition of Pr^i_2Te [R = Pr^i or Me (from Me_2Cd)].

Bu^t_2Se completely removes the problem of prereaction and may reduce the problem of N–H passivation. Previous studies had suggested, on rather limited evidence, that β-H elimination might be important.[10,44] We have used both deuterium labelling and designed precursors to study the decomposition of bis-(tertiaryalkyl)selenium compounds and find that a radical mechanism is the only one that explains all of the data. The key observations from the gas phase pyrolysis of Bu^t_2Se in He, H_2 or D_2 in the presence or absence of d^{18}-Bu^t_2Se are: (i) 2-methylpropene and 2-methylpropane are formed in a 10 : 1 ratio; (ii) neither Bu^tSeH nor H_2S are observed, although they would be stable under the decomposition conditions; (iii) the temperature profiles of the decomposition and the 2-methylpropene : 2-methylpropane ratio are essentially the same in H_2 or He; (iv) decomposition of d^{18}-Bu^t_2Se in H_2 produces C_4D_9H and C_4D_{10} (ratio 2.6 : 1); (v) co-decomposition of d^0- and d^{18}-Bu^t_2Se produces d^0, d^1, d^9 and d^{10} 2-methylpropane in the ratio 2.29 : 1 : 2.86 : 1.2.[31,32] The failure to observe 2,2,3,3-tetramethylbutane, Bu^tSeH or H_2Se effectively rules out reductive elimination or β-H abstraction.

The failure to observe 2,2,3,3-tetramethylbutane together with the observation that the 2-methylpropane : 2-methylpropene ratio ≠ 1 might also indicate that the products cannot be formed from reactions of $Bu^t\cdot$. However, at temperatures above 290 °C, the loss of H· from $Bu^t\cdot$ becomes competitive with disproportionation and combination and the proportions of both 2-methylpropane and 2,2,3,3-tetramethylbutane fall as the temperature rises.[45] This complication does not arise in the studies of Pr^i_2Te since these were carried out at 370 °C, whilst the loss of H· from $Pr^i\cdot$ is not significant below 400 °C.[27] Although the close similarity of the 2-methylpropene : 2-methylpropane ratio formed from Bu^t_2Se in He and H_2 suggests no involvement of the carrier gas, the formation of C_4D_9H from the decomposition of d^{18}-Bu^t_2Se in H_2 shows that the carrier gas can be involved.

A mechanism that would rationalise all of these observations is similar to that shown in Fig. 6 for Pr^i_2Te, with R· being $Bu^t\cdot$ or H·. In helium Se–C bond cleavage leads to $Bu^t\cdot$ and $Bu^tSe\cdot$ which immediately decomposes Se and a second $Bu^t\cdot$. $Bu^t\cdot$ then abstracts H· from Bu^t_2Se (the highest concentration species available) to give 2-methylpropane, 2 × 2-methylpropene, Se and H· (as for Pr^i_2Te, see above). H· then starts a chain reaction by abstracting H· from Bu^t_2Se. In H_2, $Bu^t\cdot$ can abstract H· from intact Bu^t_2Se or from H_2. Either way, the product ratio will be unaffected since H· continues the chain. For Pr^i_2Te, the 2 : 1 ratio of 2-methylpropene : 2-methylpropane and the increase in the proportion of 2-methylpropane in hydrogen over that obtained in helium suggests that H· does not abstract H· from intact Pr^i_2Te in this case. Calculations have shown, however that the concerted reaction similar to that shown in Fig. 6 may not occur for Bu^t_2Se, at least in the gas phase, because both $Se_{(g)}$ and H· are high energy species, but rather that it occurs in a

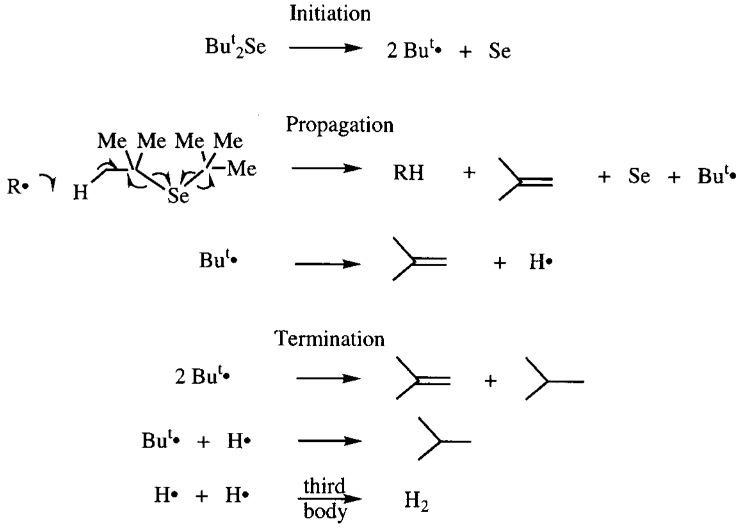

Fig. 7 Proposed mechanism for the decomposition or reaction of Bu$^t_2$Se [R = Bu^t·, Me· (from Me$_2$Zn) or H· (from decomposition of Bu^t· or from Bu^t· + H$_2$)].

stepwise manner (Fig. 7). This is very likely because H· loss from Bu^t· is important at these temperatures.[45] Using published and calculated activation parameters, it is possible to model all the observed results using this sequential mechanism.[32]

A sequence of reactions similar to that shown in Fig. 7, but with HS· as the chain carrier, accounts for the decomposition of Bu^{t}SH and it is sobering to note that this mechanism was first proposed nearly 50 years ago on the basis of careful kinetic measurements![46]

Me$_2$M (M = Cd or Zn) both undergo homolytic cleavage of the M–C bond, but in the absence of any other reagent the radicals recombine and the decomposition temperature is very high. In the presence of Bu$^t_2$Se[31,32] or Pr$^i_2$Te,[26] the methyl radicals abstract H·, in the case of Me$_2$Zn and Bu$^t_2$Se to initiate a chain reaction similar to that shown in Fig. 6, but with all the species except the hydrocarbons adsorbed on the surface of ZnSe. This reaction becomes accessible if surface bound, rather than free, Se and H· are formed. Surface bound H· carries the chain so that methane and 2-methylpropene are the major products. For Me$_2$Cd and Pr$^i_2$Te, similar reactions occur but radical coupling to give 2-methylpropene (Me· + Pr^i·), ethane (Me· + Me·) and 2,3-dimethylbutane (Pr^i· + Pr^i·) are also important. In this case, it is believed that Me· reacts with Pr$^i_2$Te by H abstraction, but also by addition to give MeTePr$^i_2$· from which Pr^i· is released, enhancing the flux of Pr^i· and forming MeTePr^i, which is an observed product and leads on to Me$_2$Te *via* Me$_2$Te$_2$.[26] Similar reactions have led us to show that MeTe^{t}Bu[47] and MeTe(allyl)[48] are not good tellurium precursors because, although Te–C bond cleavage occurs at low temperature, Me$_2$Te is very stable so that their ability to release tellurium at low temperature is limited. Interestingly, we do not see evidence for addition of Me· to Bu$^t_2$E′ (E′ = S or Se), presumably for steric reasons (bigger alkyl group, smaller chalcogenide). We do, however, observe small amounts of 2-methylpropane if the Me$_2$Zn and Bu$^t_2$Se are copyrolysed in hydrogen. In D$_2$, the 2-methylpropane is predominantly C$_4$H$_8$D$_2$ whereas Me$_2$Zn and d^{18}-Bu^{t}Se in H$_2$ give C$_4$D$_9$H$_2$, showing that the 2-methylpropane is a secondary product formed from the hydrogenation of 2-methylpropene, presumably catalysed by ZnSe.[31,32]

Photochemically at room temperature, Bu$^t_2$Se decomposes to give 2-methylpropene and 2-methylpropane (1 : 1) together with small amounts of 3,4-dimethylbutane and Bu$^t_2$Se$_2$. Co-photolysis of d^0- and d^{18}-Bu$^t_2$Se gives the same products (2-methylpropane is d^0, d^1, d^9 and d^{10}) together with d^9-Bu$^t_2$Se, suggesting that Bu^{t}Se· is stable at this temperature and that radical–radical reactions dominate. The Bu$^t_2$Se$_2$ is d^0 and d^{18} (no d^9 is formed) so it is formed by a concerted reaction between Bu$^t_2$Se and Se.[31,32]

We have also used 'reporter groups' to probe the decomposition of R$_2$E′ and RE′H (E′ = S or Se), based on the ideas elaborated above for hex-5-enyl groups[25] but extending them to include secondary (1-methylhex-5-enyl) and tertiary (1,1-dimethylhex-5-enyl) groups.[49]

For (hex-5-enyl)$_2$E′, 50% of the products are cyclic whilst the other 50% are hexa-1,3- or -2,4-dienes. As shown in Fig. 5, the cyclic products arise from E′–C bond cleavage followed by cyclisation of the formed hex-5-enyl radicals and we have concluded that the hexadienes arise from cyclisation of (hex-5-enyl)E′· to give a six- or seven-membered ring from which the dienes are produced by an unknown mechanism.[25] Abstraction of H from intact (hex-5-enyl)$_2$E′ by cyclohexyl or cyclopentyl methyl radicals, analogous to the reactions proposed for the decomposition of Bu$^t_2$Se or Pr$^i_2$Te, does not appear to be important since we largely see cyclohexene and methylenecyclopentene from *loss* of H· from the radicals. This may be rationalised because the primary alkyl groups have only a small number of β-H atoms available for abstraction. The presence of primary alkyl groups and/or the ability of (hex-5-enyl)E′· to cyclise might also explain the stability of (hex-5-enyl)E·, the similarity in the product distribution for E′ = S or Se and the high decomposition temperature of these alkyls. Reducing the number of β-H atoms reduces the probability of reaction between (hex-5-enyl)E′· and (hex-5-enyl)$_2$E′ and radical radical reactions must then become more important, thus also contributing to the higher decomposition temperatures. For (hex-5-enyl)SH, the majority of the products are the hexa-2,3- and -3,4-dienes suggesting that, in this case, S–H bond cleavage is important.

Using a similar approach but designing the hexenyl group so that it has a tertiary C atom attached to the chalcogenide, *i.e.* 1,1-dimethyhex-5-enyl (hex′), the dialkyl compounds are too involatile for gas phase studies, but we have studied the decomposition of MeE(hex′) (E = Se or Te).[49] In both cases the major hydrocarbon products are unsaturated cyclic hydrocarbons, with smaller amounts of 2-methylhepta-1,6- and -1,5-diene. (These products are more important for E = Se.) The cyclic hydrocarbons mainly contain six-membered rings, but some of them do not contain the expected geminal dimethyl group. We assume that these are secondary products caused by rearrangements at the high temperatures involved in this study. For the tellurium compound, products in which the cyclised radicals add back to MeTe· are also observed together with Me$_2$Te$_2$ and Me$_2$Te. The Se containing products are Me$_2$Se$_2$, Me$_2$Se and MeSeH. All the hydrocarbon products can be rationalised by a decomposition mechanism involving E–C

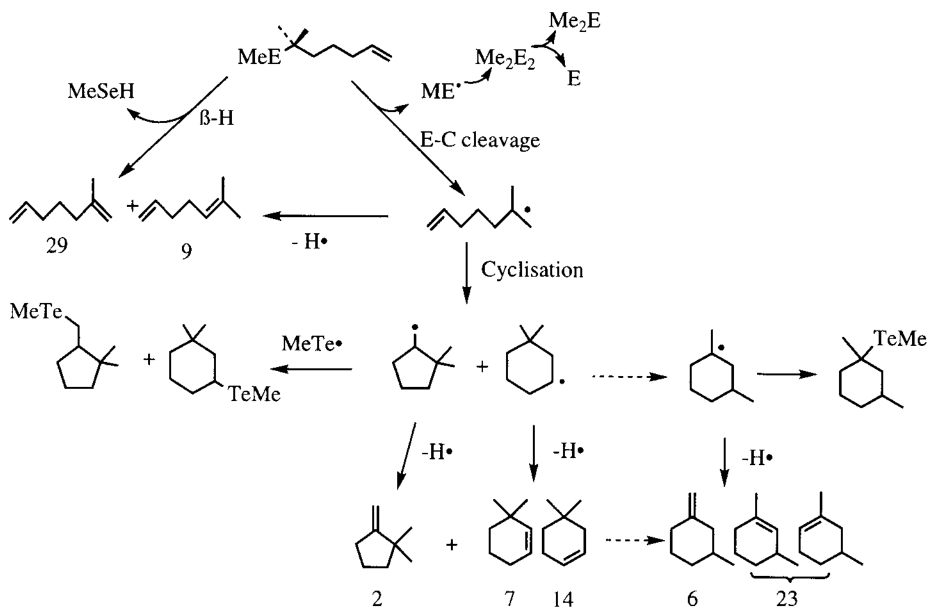

Fig. 8 Proposed mechanism for the decomposition of (1,1-dimethylhex-5-enyl)MeE (E = Se or Te). The dashed arrows indicate tentative rearrangements. Numbers shown are % of hydrocarbon products for E = Se at 450 °C in He (10% of an unknown product was also observed). For E = Te, the ratios are similar, except that much less of the straight chain products are observed indicating that β-H elimination is not important for E = Te.

cleavage followed by loss of H· from the 2-methylhept-6-en-2-yl radical before or after cyclisation (Fig. 8). However, the larger amounts of straight chain products obtained when E = Se and the observation of MeSeH show that in this case, β-H abstraction is a competing process, although its importance decreases as the temperature is raised. There is no evidence for abstraction of H from intact MeE(hex′) by any of the radicals since this would lead to saturated cyclic or monounsaturated straight chain products. None are observed. This is presumably because H· loss from these bulky radicals is expected to be dominant at the high temperatures of this study, by analogy with the reactivity of $Bu^t·$.[45]

Conclusions

Labelled and specially designed analogues of precursors are capable of giving high quality information about the processes that occur during MOVPE reactions. For primary arsines, these studies together with semi-empirical calculations show that reductive elimination of H_2 is the first step and that gas-phase adducts are not important in the reaction chemistry. For Group 16 precursors, homolytic cleavage of the C–E bond (E = S, Se or Te) occurs and detailed product analyses, especially when using labelled precursors give mechanistic details about susbequent steps in the reactions. These types of studies allow new precursors with better properties for *e.g.* low temperature growth to be designed.[50]

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Notes and references

1 P. Zanella, G. Rossetto, F. Ossola, M. Porchia and J. O. Williams, *Chem. Mater.*, 1991, **3**, 225.
2 *Metal Organic Vapour Phase Epitaxy 1996*, ed. J. B. Mullin, *J. Cryst. Growth*, 1997, **104**, and references therein.
3 H. M. Manasevit, *Appl. Phys. Lett.*, 1968, **12**, 156.
4 H. M. Manasevit and W. I. Simpson, *J. Electrochem. Soc.*, 1971, **118**, 644.
5 R. M. Lum and J. K. Klingert, *J. Cryst. Growth*, 1991, **107**, 290.
6 D. J. Cole-Hamilton, *Chem. Br.*, 1990, **26**, 852.
7 M. E. Pemble, in *Mechanisms of Reactions of Organometallic Compounds with Surfaces*, ed. D. J. Cole-Hamilton and J. O. Williams, Plenum, New York, 1989, p. 145.
8 J. S. Foord, C. L. French, C. L. Levoguer, G. J. Davies and P. J. Skevington, *Semiconduct. Sci. Technol.*, 1993, **8**, 959.
9 J. E. Hails, *Adv. Mater. Opt. Electron.*, 1994, **3**, 151.
10 G. H. Fan, N. Maung, T. L. Ng, P. F. Heelis, J. O. Williams, A. C. Wright, D. F. Foster and D. J. Cole-Hamilton *J. Cryst. Growth*, 1997, **170**, 485.
11 S. H. Li, C. A. Larsen, N. I. Buchan, G. B. Stringfellow, W. P. Kosar and D. W. Brown, *J. Appl. Phys.*, 1989, **65**, 5161 and references therein.
12 R. H. Marking, W. L. Gladfelter and K. F. Jensen, *Chem. Mater.*, 1990, **2**, 499.
13 D. F. Foster, C. Glidewell and D. J. Cole-Hamilton, *Appl. Phys. Lett.*, 1993, **63**, 57.
14 D. F. Foster, C. Glidewell and D. J. Cole-Hamilton, *J. Electron. Mater.*, 1994, **23**, 69.
15 D. F. Foster, C. Glidewell, G. R. Woolley and D. J. Cole-Hamilton, *J. Electron. Mater.*, 1995, **24**, 1731.
16 D. F. Foster, C. Glidewell and D. J. Cole-Hamilton, *Appl. Phys. Lett.*, 1993, **63**, 214.
17 D. F. Foster, C. Glidewell, D. J. Cole-Hamilton, I. M. Povey, R. D. Hoare and M. E. Pemble, *J. Cryst. Growth*, 1995, **145**, 104.
18 R. D. Hoare, M. E. Pemble, I. M. Povey, J. O. Williams, D. F. Foster, C. Glidewell and D. J. Cole-Hamilton, *J. Cryst. Growth*, 1994, **137**, 347.
19 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 137.
20 A. S. Gordon and S. R. Smith, *J. Phys. Chem.*, 1962, **66**, 521.
21 J. E. Hails, I. Girling and D. R. Stern, *Mater. Res. Soc. Symp. Proc.*, 1991, **204**, 155.
22 J. Stevenson, W. Bell, J. Ferry, D. J. Cole-Hamilton and J. E. Hails, *J. Organomet. Chem.*, 1993, **449**, 141.
23 H. Lemkuhl, I. Döring and H. Nehr, *J. Organomet. Chem.*, 1981, **221**, 7.
24 W. Bell, E. A. D. McQueen, J. C. Walton, D. F. Foster and D. J. Cole-Hamilton, *J. Cryst. Growth*, 1992, **117**, 58.
25 D. F. Foster, W. Bell, J. Stevenson, D. J. Cole-Hamilton and J. E. Hails, *J. Cryst. Growth*, 1994, **145**, 520.
26 W. Bell, J. Stevenson, D. J. Cole-Hamilton and J. E. Hails, *Polyhedron*, 1994, **13**, 1253.
27 J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1969, **55**, 921.

28 W. Bell, D. J. Cole-Hamilton, P. N. Culshaw, A. E. D. McQueen, D. V. Shenai-Khatkhate, J. C. Walton and J. E. Hails, *J. Organomet. Chem.*, 1992, **430**, 43.
29 A. E. D. McQueen, P. N. Culshaw, J. C. Walton, D. V. Shenai-Khatkhate, D. J. Cole-Hamilton and J. B. Mullin, *J. Cryst. Growth*, 1991, **107**, 325.
30 D. F. Foster, N. L. Pickett and D. J. Cole-Hamilton, *Silicon, Phosphorus Sulfur*, 1998.
31 N. L. Pickett, D. F. Foster and D. J. Cole-Hamilton, *Proc. Electrochem. Soc. Conf.*, 1998, in press.
32 N. L. Pickett, D. F. Foster, D. Ellis, N. Maung, J. E. Hails and D. J. Cole-Hamilton, *J. Mater. Chem.*, to be submitted.
33 P. J. Wright, B. Cockayne, P. J. Parbrook, P. E. Oliver and A. C. Jones, *J. Cryst. Growth*, 1991, **108**, 525 and references therein.
34 A. Kamata, M. Mitsuhashi and H. Fujita, *Appl. Phys. Lett.*, 1993, **63**, 3353.
35 N. L. Pickett, D. F. Foster and D. J. Cole-Hamilton, *J. Mater. Chem.*, 1996, **6**, 507.
36 N. L. Pickett, D. F. Foster and D. J. Cole-Hamilton, *J. Cryst. Growth*, 1997, **170**, 476.
37 N. L. Pickett, F. G. Riddell, D. F. Foster, D. J. Cole-Hamilton and J. R. Fryer, *J. Mater. Chem.*, 1997, **7**, 1855.
38 X. Li, J. R. Fryer and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1994, 1715.
39 S. W. Haggata, X. Li, D. J. Cole-Hamilton and J. R. Fryer, *J. Mater. Chem.*, 1996, **6**, 1771.
40 S. W. Haggata, D. J. Cole-Hamilton and J. R. Fryer, *J. Mater. Chem.*, 1997, **7**, 1969.
41 D. N. Armitage, H. M. Yates, J. O. Williams, D. J. Cole-Hamilton and I. L. J. Patterson, *Adv. Mater. Opt. Electron.*, 1992, **1**, 43.
42 D. F. Foster, I. L. J. Patterson, L. D. James, D. J. Cole-Hamilton, D. N. Armitage, H. M. Yates, A. C. Wright and J. O. Williams, *Adv. Mater. Opt. Electron.*, 1994, **3**, 163.
43 N. L. Pickett, S. Lawson, W. G. Thomas, F. G. Riddell, D. F. Foster, D. J. Cole-Hamilton and J. R. Fryer, *J. Mater. Chem.*, 1998, **8**, 2769.
44 W. S. Kuhn, R. Helbing, B. Qu'Hen and O. Gorochov, *J. Cryst. Growth*, 1995, **146**, 580.
45 R. N. Birrell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 4218.
46 C. G. Thompson, R. A. Meyer and J. S. Ball, *J. Am. Chem. Soc.*, 1952, **74**, 3284.
47 J. E. Hails, D. J. Cole-Hamilton and W. Bell, *J. Cryst. Growth*, 1994, **145**, 596.
48 J. E. Hails, D. J. Cole-Hamilton and A. E. D. McQueen, *J. Cryst. Growth*, 1998, **183**, 594.
49 D. F. Foster, J. E. Hails and D. J. Cole-Hamilton, unpublished observations.
50 W. Bell, J. Stevenson, J. E. Hails, D. Ellis and D. J. Cole-Hamilton, unpublished observations.

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