Russian Chemical Reviews **64** (10) 953–966 (1995) ©1995 Russian Academy of Sciences and Turpion Ltd

UDC 541.124-13 : 547,25

Kinetics of the thermal decomposition of alkyl derivatives of Group III and V elements

V A Yablokov, N V Yablokova

Contents

I.	Introduction	953
II.	Kinetics of the thermal decomposition of alkyl derivatives of Group III elements	954
III.	Kinetics of the thermal decomposition of alkyl derivatives of Group V elements	958
IV.	Joint decomposition of the organoelement compounds and hydrides of Group III and V elements in the gas phase and under the conditions for the formation of epitaxial layers	960
V.	Conclusion	964

Abstract. The results of kinetic studies on the thermal decomposition of alkyl derivatives of Group III and V elements, used to obtain semiconducting epitaxial structures, are surveyed. Their reaction paths in the gas phase and on the surface of epitaxial layers as well as the factors influencing the mode of decomposition are analysed. The possibility of the formation of complexes between the components of the organoelement mixture during their joint pyrolysis is demonstrated. The bibliography includes 128 references.

I. Introduction

Organometallic compounds (OMC) and hydrides are used as a source of the metal in the formation of epitaxial layers of semiconducting materials.[1–3] The decomposition of the OMC and hydrides on the surface, known as the OMC method or as the metal organic chemical vapour deposition (MOCVD) or the metal organic vapour phase epitaxy (MOVPE) method, is undoubtedly an effective technological process, which makes it possible to achieve the selective growth of epitaxial layers with the required composition and thickness and the necessary set of properties.[4,5] Manasevit was the first to propose the use of the reaction of trimethylgallium with arsine in order to obtain epitaxial gallium arsenide layers.[6,7] This reaction can be formulated by means of the following overall expression:

$$(CH_3)_3Ga + AsH_3 = GaAs + 3CH_4.$$

In subsequent studies,[8,9] the method was used to grow films of organoelement compounds (OEC) of Group III–V elements. This procedure was used to obtain GaP films from $(CH_3)_3Ga$ and PH_3, GaAsP films from $(CH_3)_3Ga$, PH_3, and AsH_3, GaAsSb films from $(CH_3)_3Ga$, SbH_3, and AsH_3, etc. AlAs, GaN, AlN, $GaAs_xP_{1-x}$, $GaAs_xSb_{1-x}$, InAs, GaInAs, InAsP, InP, etc. films, based on the alkyl derivatives of Group III elements and nitrogen, phosphorus, arsenic, and antimony hydrides, have been grown similarly.[8,9]

Initially the investigators were interested exclusively in the technological problems associated with the construction of the reactors, the behaviour of the carrier gas, and the selection of the substances required, problems of mass transfer and hydrodynamic aspects being discussed.[9–11] At the present time, serious attention has been devoted to the fundamental principles of these technological processes: the mechanisms of the chemical reactions occurring in the gas phase and on the surface.[12–14] In his review,[5] Shaw distinguishes the following stages in the MOCVD process: (1) the supply of the reactants to the film growth region; (2) diffusion of the reactants to the surface of the support; (3) adsorption of the reactants on the surface; (4) surface processes involving chemical reactions, surface diffusion, and the binding of deposited materials to the support; (5) desorption of the gaseous chemical reaction products; (6) diffusional transport of the products in the stream of carrier gas; (7) removal of the reaction products from the growth region.

Stages 3–5 generally determine the rate of the deposition process and its principal physicochemical characteristics. In the chain of problems comprising the synthesis, purification, and stabilisation of the OEC, the kinetics, thermodynamics, and mass transfer of the OEC, and the design features of the reactors for the growing of epitaxial layers, each has independent importance. However, it is recognised that the factor inhibiting the development of the chemical gas-phase deposition is primarily the difficulties of understanding the mechanism of the pyrolysis of the OEC.[12–14]

In the present review, attention is concentrated on the consideration of the mechanisms and rates of the thermal decomposition reactions of the OEC of Group III and V elements in the gas phase and under the real conditions in the growth of films as a result of chemical deposition from the gas phase. The study of the kinetics of the thermal decomposition of the above classes of compounds is of theoretical interest for the development of the OEC chemistry and ensures the solution of the technological problems in the preparation of Group III–V semiconducting materials.

The pyrolysis of the OEC to the element and hydrocarbons is a complex chemical process. The multistage nature of the homolytic reactions involving the abstraction of alkyl groups from the initial and intermediate OEC is combined with molecular decomposition reactions (β-elimination). The homogeneous and heterogeneous stages are manifested in different ways

V A Yablokov Department of Chemistry, Nizhnii Novgorod State Academy of Civil Engineering, ul. Il'inskaya 65, 603600 Nizhnii Novgorod, Russian Federation. Fax (7-831) 234 02 01
N V Yablokova Institute of Chemistry, Lobachevskii Nizhnii Novgorod State University, prosp. Gagarina 23, korp. 5, 603600 Nizhnii Novgorod, Russian Federation. Fax (7-831) 235 64 80

Received 21 April 1995
Uspekhi Khimii **64** (10) 1017–1030 (1995); translated by A K Grzybowski

in the pyrolytic reactions. As a consequence of the dual action of the wall, which is involved in the initiation and the destruction of the active centres on the surface, cases are possible where, despite the presence of heterogeneous stages, the rate of the overall process is independent of the ratio of the surface area of the walls (S) to the volume (V) of the reactor.

The homogeneous-heterogeneous character of the pyrolysis of the OEC and the involvement of these compounds in radical and molecular consecutive-parallel elementary reactions is the principal reason why it is impossible to establish a chemical mechanism which corresponds to the experimentally established macrokinetic law. Nevertheless, the knowledge of the macrokinetic laws makes it possible to solve a series of general and specific problems — in the first place, to test the validity of the hypotheses concerning the reaction mechanisms. The postulated mechanism is tested by comparing the experimental and theoretical and kinetic laws. The discrepancy between experiment and theory is a reliable sign that the proposed mechanism is erroneous. On the other hand, consistency between theory and experiment is not a sufficient basis for the adoption of the postulated mechanism.

Furthermore, the knowledge of the macrokinetics makes it possible to distinguish certain characteristic features of the reaction investigated. Thus a fractional order with respect to the OEC concentration and the independence of the rate of reaction of the concentration of one of the reactants yield reliable information about the involvement of free radicals in the reaction and about the role of the reactants in the rate-limiting stage of the process. Here one should also include the determination of the heterogeneity factor (S/V). The variation of the rate of the overall reaction as a function of S/V indicates an appreciable contribution of the desorption process (the fifth stage) and of the reactions at the interface.

There have been fairly numerous kinetic measurements on the pyrolysis of OEC of Group III and V elements, but they are frequently contradictory. Systematic treatment and discovery of the general features of the variation of the reactivity of individual OEC and their mixtures in the gas state and under the conditions of the growth of epitaxial layers will make it possible to select keys to the regulation of these processes.

II. Kinetics of the thermal decomposition of alkyl derivatives of Group III elements

The most 'puzzling' OEC among the compounds of Group III elements are probably organoaluminium compounds and particularly $(CH_3)_3Al$. The formal kinetics of its thermal decomposition were investigated for the first time by Yeddanapalli et al.[15] In the temperature range 570–610 K, the rate of thermal decomposition of $(CH_3)_3Al$ is described by the equation for a reaction the order of which is 3/2. The rate constant can be expressed as follows:

$$k = 8.1 \times 10^{15} \exp\left(-\frac{188.3}{RT}\right).$$

It is independent of the initial pressure of the gaseous $(CH_3)_3Al$ in the pressure range $(0.2-1.14) \times 10^4$ Pa. The variation of S/V hardly affects the constant k. The principal gaseous reaction product is methane (91 vol.%–98 vol.%). In the presence of hydrogen, the activation energy (here and henceforth E is expressed in kJ mol^{-1}) for the $(CH_3)_3Al$ decomposition reaction decreases from 188.3 to 127.6 kJ mol^{-1}. The numerical values of the rate constants decrease under these conditions, while the reaction order remains 3/2.

In later studies,[12,16] it was reported that the pyrolysis of $(CH_3)_3Al$ is first order with respect to the organoaluminium compound.

The reaction was carried out under a hydrogen atmosphere (10^5 Pa), where the partial pressure of $(CH_3)_3Al$ was ~200 Pa. The pressure was sufficiently low to allow the virtual exclusion of the sensitised decomposition of the OEC.

$$(CH_3)_3Al + \dot{C}H_3 \longrightarrow (CH_3)_2Al\dot{C}H_2 + CH_4$$

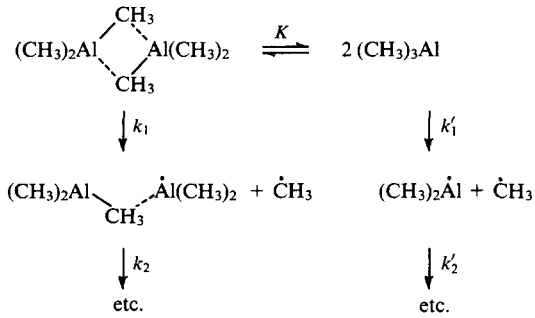
A distinctive feature of the pyrolysis of $(CH_3)_3Al$ at 200 Pa is the existence of 'high-temperature' (450–550 K)[12] and 'low-temperature' (290–320 K)[16] reaction regions. Activation energies for pyrolysis of 158.6 and 37.6 kJ mol^{-1} correspond respectively to these regions. In a general form, the 'low-temperature' pyrolysis is considered as a system of consecutive parallel reactions, where the first stage is the thermal decomposition of the trimethylaluminium dimer.[16]

$$[(CH_3)_3Al]_2 \xrightarrow{k_1} 2\,\dot{C}H_3 + [(CH_3)_2Al]_2$$

The low activation energy for the 'low-temperature' pyrolysis can be explained[16] by the fact that the bonds between the bridging methyl groups of the dimeric compound and the aluminium atom are weaker than the bonds in the monomeric molecule: the bond strength in the latter has been estimated, according to the data in Tel'noi's book,[17] as 278 ± 4 kJ mol^{-1}. The concentration of dimeric trimethylaluminium at 290–425 K is known[18] to exceed or be comparable to the concentration of the monomer, so that the dimers may play a significant role in the 'low-temperature' macrokinetics. However, this is not the only possible explanation of the characteristic features of the 'low-temperature' pyrolysis. Studies on the kinetics of the decomposition of trimethylaluminium on hot solid surfaces of copper and aluminium at 295–880 K demonstrated that methyl radicals are predominantly formed during the reaction.[19] The energy for the generation of methyl radicals in the interaction of $(CH_3)_3Al$ with the aluminium surface is 46 ± 8 kJ mol^{-1}. Within the limits of the error of the measurement, this quantity agrees with the activation energy for the 'low-temperature' pyrolysis (37.6 kJ mol^{-1}) quoted by Suzuki et al.[16] It is entirely probable that at 290–425 K the source of methyl radicals may be the dimeric trimethylaluminium, which decomposes heterogeneously at the surface.

With increase in temperature, the fraction of trimethylaluminium dimers diminishes as a result of dissociation. Therefore, over a wide temperature range it is necessary to take into account the contributions to the overall process by both the dimeric and monomeric forms (Scheme 1).

Scheme 1



T/K	E/kJ mol^{-1}	Ref.
290–450	37.6	16
450–565	158.6	12
570–610	188.3	15

The role of each of the competing paths in the pyrolysis is determined by two temperature-dependent factors: the shift of the dimer ⇌ monomer equilibrium (K) and the change in the rate constants for the abstraction of the methyl groups from the dimer (k_1) and the monomer (k_1'). The higher the reaction temperature, the higher the activation energy for the pyrolysis of $(CH_3)_3Al$.

This type of variation of E is consistent with the concept of competing reactions occurring with rate constants k_i and k_i', where $i = 1, 2$ (see Scheme 1).

The monomer concentration increases with increasing temperature. The rate constant for the decomposition of the monomer (k_1') increases with temperature faster than the rate constant for the composition of the dimer (k_1). In the ideal case, the complete conversion of the dimer into the monomer can be achieved by raising the temperature. If the rate-limiting stage is the abstraction of the first methyl group from the $(CH_3)_3Al$ molecule, then the value of E at temperatures above 600 K should approach the average bond dissociation energy $D_{Al-CH_3} = 278$ kJ mol^{-1}. An increase in the length of the hydrocarbon group virtually rules out the possibility of the existence of the dimeric form of the organoaluminium compound in the gas phase.[18,20] The nature of the pyrolysis products then changes. The contribution of the molecular β-elimination reaction increases. With increase in the length of the hydrocarbon group R, the thermal stability of the organoaluminium compounds falls.

$$R_3Al \begin{cases} \longrightarrow R_2AlH + R'CH{=}CH_2 & (1) \\ \longrightarrow R_2\dot{A}l + \dot{R} & (2) \end{cases}$$

For example, the rate of the gas-phase decomposition of $(C_2H_5)_3Al$ ($P_0 = 6.7 \times 10^3$ Pa, T = 435 – 465 K) is appreciably higher than the rate of decomposition of $(CH_3)_3Al$.[21] The temperature dependence of the effective rate constant for the overall $(C_2H_5)_3Al$ reaction is given by the equation[21]

$$k = 10^{8.2} \exp\left(-\frac{121.3}{RT}\right).$$

The attainment of a limiting value of the rate constant for the gas-phase decomposition of the organoaluminium compounds R_3Al on passing from $R = C_2H_5$ to $R = n-C_8H_{17}$ is indicated indirectly by data on the liquid-phase thermal decomposition of R_3Al.[22] The rate constants for the liquid-phase thermal decomposition of $(n\text{-}C_4H_9)_3Al$ and $(n\text{-}C_8H_{17})_3Al$ differ only slightly (1.5×10^{-4} s^{-1} and 1.7×10^{-4} s^{-1} respectively).

The thermal decomposition of the gaseous alkylgallium compound R_3Ga ($R = CH_3$, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$) obeys the kinetic equation for a first-order reaction.[13,14,23–32] Trimethylgallium exhibits the highest thermal stability. The homolysis of the Ga–C bond with a fairly ready loss of two methyl groups is characteristic of this compound.[23,26,28] The rate-limiting stage of the process is the abstraction of the first methyl group.

$$(CH_3)_3Ga \longrightarrow (CH_3)_2\dot{G}a + \dot{C}H_3$$

The subsequent fate of the methyl radicals depends on the composition of the gas phase. The reaction

$$C_6H_5CH_3 + \dot{C}H_3 \longrightarrow C_6H_5\dot{C}H_2 + CH_4,$$

is observed in a stream of toluene. The bibenzyl formed confirms the radical mechanism of the decomposition of $(CH_3)_3Ga$ in a toluene atmosphere.[23]

Mass-spectrometric analysis of the gas phase[14] confirms the occurrence of the following reactions of the methyl radicals:[14]

$$\dot{C}H_3 + \dot{C}H_3 + M \longrightarrow C_2H_6 + M^*$$

$$\dot{C}H_3 + H_2(D_2) \longrightarrow CH_4(CH_3D) + \dot{H}(\dot{D})$$

$$\dot{C}H_3 + (CH_3)_3Ga \longrightarrow CH_4 + (CH_3)_2Ga\dot{C}H_2$$

M= reactor wall or any molecule.

In a stream of hydrogen, the decomposition is faster than in a stream of helium, which suggests the possibility of the occurrence of the reaction

$$(CH_3)_3Ga + \dot{H} \longrightarrow (CH_3)_2\dot{G}a + CH_4.$$

At a temperature below 720 K, the polymer $(GaCH_x)_n$ is formed.[26] Above 770 K, it decomposes with liberation of metallic gallium.

One may agree with the claim that hydrogen reduces the activation energy by the abstraction of the last methyl group in the final stage of the pyrolysis.[13] The dissociation of the bond in monomethylgallium requires an energy of approximately 343 kJ mol^{-1}.[33] The overall activation energy for the decomposition of $(CH_3)_3Ga$ in a stream of hydrogen is in the range 184–260 kJ mol^{-1} according to the data of different workers.[25,26] The concluding stage of the decomposition of $(CH_3)_3Ga$ in the gas phase should therefore be a reaction favoured energetically.[34]

$$CH_3Ga{:} + H_2 (\text{or } \dot{H}) \longrightarrow Ga + CH_4 + \dot{H}$$

An attempt to detect the presence of gallium atoms in the vapour-phase decomposition of $(CH_3)_3Ga$ by IR spectroscopy was unsuccessful.[35] At any rate the pyrolytic reactions catalysed by the surface or occurring on the surface do not limit the rate of the process,[26,36] since an increase in the surface area does not accelerate the pyrolysis of $(CH_3)_3Ga$.

The homogeneous-heterogeneous mechanism of the decomposition of $(CH_3)_3Ga$, examined in detail by Masi et al.,[36] has been proposed on the basis of studies of the decomposition of this compound under the conditions of the formation of epitaxial layer by the MOCVD method,[23,28–30] while a model mechanism has been proposed on the basis of data on the pyrolysis of $(CH_3)_3Ga$ at different temperatures and the involvement of H_2 in the decomposition processes and in the processes leading to the formation of the decomposition products in the gas phase and on the GaAs surface. It was established that, in the gas-phase decomposition of $(CH_3)_3Ga$ in a stream of hydrogen, the gallium hydrides $[H_xGa(CH_3)_{3-x}]$ are not formed, especially under the conditions for the growth of GaAs films. The absence of the dissociation of $(CH_3)_3Ga$ in the gas phase to metallic gallium has been confirmed by spectroscopic data, according to which the concentration of gallium atoms in the gas phase is several orders of magnitude lower than the concentration of the intermediate species $CH_3Ga{:}$. Spectroscopic studies[37,38] made it possible to consider in detail the surface reactions of $(CH_3)_3Ga$, which include the dissociation of $(CH_3)_3Ga$ and of the intermediate species $(CH_3)_2Ga^*$ and $CH_3Ga{:}$ on the surface adsorption centres (s).[36] The activation parameters were estimated for each of the reactions presented below, which makes it possible to predict their occurrence in the real MOCVD process (Scheme 2).

Reactions (3)–(6) take place in the gas phase, whilst reactions (7)–(13) occur on the surface. The activation energies E are given in kJ mol^{-1} and the rate constants k in (mol cm^{-3})$^{1-n}$s^{-1}, where n is the reaction order.

The epitaxial GaAs layers were grown by the MOCVD method on a base comprising $(CH_3)_3Ga$ and metallic arsenic using hydrogen as the carrier gas.[39] Methane molecules are obtained in this process via two paths: via the direct gas-phase interaction of two methyl radicals [see Eqn (44) below], formed on decomposition of $(CH_3)_3Ga$, and via the reaction of the $\dot{C}H_3$ radical with the carrier gas. The activation energies for these processes were estimated as 23 and 39 kJ mol^{-1} respectively.

The reaction involving the abstraction of alkyl radicals, typical for $(CH_3)_3Ga$, is also characteristic of $(C_2H_5)_3Ga$ with the sole difference that in the case of the latter β-elimination takes place as a parallel reaction. The probable mechanism of

Scheme 2

$$(CH_3)_3Ga \longrightarrow (CH_3)_2\dot{G}a + \dot{C}H_3, \qquad k = 3.5 \times 10^5 \exp\left(-\frac{249}{RT}\right); \tag{3}$$

$$(CH_3)_2\dot{G}a \longrightarrow CH_3Ga{:} + \dot{C}H_3, \qquad k = 8.7 \times 10^7 \exp\left(-\frac{148}{RT}\right); \tag{4}$$

$$(CH_3)_3Ga + \dot{H} \longrightarrow (CH_3)_2\dot{G}a + CH_4, \qquad k = 5 \times 10^{13} \exp\left(-\frac{41.9}{RT}\right); \tag{5}$$

$$(CH_3)_2\dot{G}a + \dot{H} \longrightarrow CH_3Ga{:} + CH_4, \qquad k = 5 \times 10^{13} \exp\left(-\frac{41.9}{RT}\right); \tag{6}$$

$$CH_3Ga{:} + Ga\,(s) \longrightarrow CH_3Ga\,(s), \qquad k = 5.4 \times 10^{11} T^{0.5}; \tag{7}$$

$$CH_3Ga\,(s) \longrightarrow CH_3Ga{:} + Ga\,(s), \qquad k = 10^{14} \exp\left(-\frac{188}{RT}\right); \tag{8}$$

$$CH_3Ga\,(s) \longrightarrow Ga\,(s) + \dot{C}H_3, \qquad k = 2.6 \times 10^{13} \exp\left(-\frac{159}{RT}\right); \tag{9}$$

$$Ga\,(s) + \dot{C}H_3 \longrightarrow CH_3Ga\,(s), \qquad k = 1.3 \times 10^{12} T^{0.5} \tag{10}$$

$$Ga\,(s) + \dot{C}H_3\,(s) \longrightarrow GaCH_3\,(s) + s, \qquad k = 10^{17} \exp\left(-\frac{41.9}{RT}\right); \tag{11}$$

$$(CH_3)_2\dot{G}a + s \longrightarrow CH_3Ga\,(s) + \dot{C}H_3, \qquad k = 5 \times 10^{11} T^{0.5}; \tag{12}$$

$$(CH_3)_3Ga + s \longrightarrow CH_3Ga\,(s) + 2\dot{C}H_3 \qquad k = 4.6 \times 10^{11} T^{0.5} \exp\left(-\frac{41.9}{RT}\right). \tag{13}$$

the decomposition of $(C_2H_5)_3Ga$, investigated by the mass-spectrometric method in a stream of He and H_2,[14] may be represented by the reactions

$$(C_2H_5)_3Ga \longrightarrow (C_2H_5)_2\dot{G}a + CH_3\dot{C}H_2 \tag{14}$$

$$(C_2H_5)_3Ga \longrightarrow (C_2H_5)_2GaH + C_2H_4 \tag{15}$$

$$2CH_3\dot{C}H_2 + M \longrightarrow C_4H_{10} + M^*, \tag{16}$$

$$CH_3\dot{C}H_2 + H_2 \longrightarrow C_2H_6 + \dot{H}, \tag{17}$$

$$CH_3\dot{C}H_2 + (C_2H_5)_3Ga \longrightarrow C_2H_6 + (C_2H_5)_2Ga\dot{C}HCH_3 \tag{18}$$

M = reactor wall or any molecule.

The radical recombination reaction (16) proceeds virtually with zero activation energy. Reaction (17) has an activation energy of 55 kJ mol^{-1}.[40] With increase in temperature, the fraction of ethene in the reaction products increases and above 600 K the elimination reaction (15) becomes the dominant path.

Quantum-mechanical calculations[41] demonstrated that the β-elimination reaction is favoured energetically for $(C_2H_5)_3Ga$ compared with the homolysis of the Ga–C bond, which agrees with the results of experimental measurements at temperatures above 600 K.

The kinetics of the pyrolysis of the alkylindium derivatives R_3In, where $R = C_2H_5$, n-C_4H_9, n-C_5H_{11}, or n-C_6H_{13}, have been investigated.[42–45] Analysis of the literature data permits the conclusion that the pyrolysis of the alkylindium derivatives in the gas phase in the temperature range 473–780 K is described by the kinetic equation for a first-order reaction. The apparent activation energy for the process decreases on passing from the methyl derivative (197.5 kJ mol^{-1}) to the hexyl derivative (63.2 kJ mol^{-1}). It was established that the pyrolysis of trialkylindium is a complex homogeneous-heterogeneous process, which proceeds simultaneously via radical and olefinic-hydride mechanisms, the radical reaction paths predominating. The formal process mechanism can be represented as follows:

$$R_3In \longrightarrow R_2\dot{I}n + \dot{R}$$

$$\downarrow$$

$$In + 2\dot{R}$$

$$2\dot{R} \longrightarrow RH + R_{(-H)}$$

$$2\dot{R} \longrightarrow R_2$$

$$\dot{R} + R_3In \longrightarrow RH + RIn\dot{R}_{(-H)}$$

$$\dot{R} \xrightarrow{In} R_{(-H)} + \dot{H}$$

$$R_3In \longrightarrow R_2InH + R_{(-H)}$$

$$2R_2\dot{I}n \longrightarrow R_2InInR_2 \longrightarrow R_2In\dot{I}nR + \dot{R}.$$

The pyrolysis $(CH_3)_3In$ at atmospheric pressure in a stream of helium or hydrogen (deuterium) has been studied in detail by the mass-spectrometric method.[45] The rate constant for the pyrolysis of $(CH_3)_3In$ in a stream of helium is comparable to the rate constants published recently and obtained in the presence of a radical trapping agent (toluene).[44]

$$\lg k = 17.9 - \frac{226}{2.3RT}$$

Trimethylindium decomposes predominantly homolytically in a stream of helium and does not undergo radical attack by methyl radicals. The pyrolysis is accelerated slightly in a stream of H_2 or D_2.

$$\lg k = 13.4 - \frac{167}{2.3RT} \qquad \text{(in a stream of } D_2\text{)},$$

$$\lg k = 15.0 - \frac{178}{2.3RT} \qquad \text{(in a stream of } H_2\text{)}.$$

The principal pyrolysis products are CH_3D and C_2H_6 in a stream of D_2 and CH_4 and C_2H_6 in a stream of H_2. The ratio CH_3D/C_2H_6 decreases monotonically with increase in temperature. In the study of the mechanism of the decomposition of $(CH_3)_3In$ in a stream of D_2, the authors[45] used a modelling procedure. It was postulated that the hypervalent short-lived

intermediate $[D(CH_3)_3In]^{\cdot}$ is formed initially.

$$\dot{D} + (CH_3)_3In \longrightarrow [D(CH_3)_3In]^{\cdot}$$

$$\dot{C}H_3 + [D(CH_3)_3In]^{\cdot} \longrightarrow CH_3D + (CH_3)_3In$$

$$\dot{D} + [D(CH_3)_3In]^{\cdot} \longrightarrow D_2 + (CH_3)_3In$$

$$[D(CH_3)_3In]^{\cdot} \longrightarrow CH_3D + 2\dot{C}H_3 + In$$

This model explains the increase in the rate of pyrolysis of $(CH_3)_3In$ in a D_2 atmosphere. A similar decomposition mechanism has also been proposed for a H_2 atmosphere.

New organometallic sources of metallic indium have been investigated—$C_2H_5(CH_3)_2In$ and $(CH_3)_2N(CH_2)_3In(CH_3)_2$. These are potential substitutes for $(CH_3)_3In$.[46,47] In contrast to $(CH_3)_3In$, these compounds are liquid at room temperature with relatively high vapour pressures. It is particularly effective to employ them in combination with *tert*-$C_4H_9PH_2$ for the preparation of high-quality InP films. $(C_2H_5)_2InCl$, which is converted into InCl on decomposition, is very effective in organometallic gas-phase epitaxy. When PH_3 and *tert*-$C_4H_9PH_2$ are used, phosphorus is incorporated during the growth of InP films.

The pyrolysis of $(CH_3)_3Tl$ has been investigated in a flow system in a stream of toluene in the temperature range 452–536 K.[48] The CH_4, C_2H_6, and $C_6H_5C_2H_5$ found in the reaction products are formed from the methyl radicals abstracted from $(CH_3)_3Tl$.

$$(CH_3)_3Tl \longrightarrow (CH_3)_2\dot{T}l + \dot{C}H_3$$

$$\downarrow$$

$$Tl + 2\dot{C}H_3$$

The apparent activation energy of 152.3 kJ mol^{-1} corresponds to the Tl–C bond dissociation energy.[48]

The kinetic parameters of the thermal decomposition of the alkyl derivatives of Group III elements are presented in Table 1. There is no unanimity as regards the estimation of the effective rate constants for the overall reactions. The constants k based on the data of different workers differ significantly for the same compound. The studies of Price and coworkers,[23,44,48,49] where the thermal stabilities of the compounds $(CH_3)_3E$ (E = Ga, In, Tl) were investigated under comparable conditions, merit special attention. The reactivities of such organometallic compounds increase in the sequence $(CH_3)_3Ga < (CH_3)_3In < (CH_3)_3Tl$. $(CH_3)_3Al$ 'deviates' from this series. Relatively low activation energies[12,15,16] and a low thermal stability, consistent with the hypothesis that its dimeric form is involved in the process kinetics, are characteristic of this compound.

The causes of the variation of the reactivity of the compounds R_3Ga in the sequence $CH_3 < C_2H_5 <$ n-$C_4H_9 <$ n-C_3H_7 [13,24,49] and of R_3In in the sequence $CH_3 <$ n-$C_4H_9 < C_2H_5 \approx$ n-$C_5H_{11} \ll$ n-C_6H_{13} [43,44] so far remain unelucidated.

It has been shown comparatively recently[50–54,55] that high-quality thin aluminium and gallium films may be obtained when complexes of aluminium and gallium hydrides with the tertiary amines $EH_3 \cdot NR_3$, where E = Al or Ga and R = CH_3 or C_2H_5, are used as the organometallic sources.[55] Such adducts do not contain an E–C bond, are less combustible and toxic than the compounds R_3E, and their vapour pressures are sufficient to employ them in the MOCVD processes at relatively low temperatures.

The thermal decomposition of the complexes $AlH_3 \cdot NR_3$, where R = CH_3 or C_2H_5, has been investigated.[56] The gas-phase decomposition leads to the formation of hydrogen, metallic aluminium, and the corresponding amine. In the condensed phase, the thermal decomposition in the temperature range 353–393 K is accompanied by the formation of the amine and a solvated polymeric form of aluminium hydride. The decomposition mechanism can be expressed as follows:

$$AlH_3 \cdot NR_3\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AlH_3\,(g) + NR_3\,(g), \qquad (19)$$

$$AlH_3\,(g) \xrightarrow{k_2} Al\,(s) + 1\tfrac{1}{2}H_2\,(g), \qquad (20)$$

$$AlH_3 \cdot NR_3\,(l) \longrightarrow \frac{n-1}{n}NR_3\,(g) + \frac{1}{n}[(AlH_3)_n \cdot NR_3]\,(s), \qquad (21)$$

$$\frac{1}{n}[(AlH_3)_n \cdot NR_3]\,(s) \longrightarrow Al\,(s) + 1\tfrac{1}{2}H_2\,(g) + \frac{1}{n}NR_3\,(g). \qquad (22)$$

The abbreviations g, l, and s correspond to the gas, liquid, and solid phases.

The following expressions were obtained for k_1 and k_2 (s^{-1}):

$$k_1 = 1.6 \times 10^{12}\exp\left(-\frac{117.2}{RT}\right) \quad \text{for } AlH_3 \cdot N(CH_3)_3,$$

$$k_1 = 5.3 \times 10^{12}\exp\left(-\frac{113}{RT}\right) \quad \text{for } AlH_3 \cdot N(C_2H_5)_3,$$

$$k_2 = 4.2 \times 10^{20}\exp\left(-\frac{175.8}{RT}\right).$$

Table 1. Parameters of the thermal decomposition of the alkyl derivatives of Group III elements.

Compound	T/K	$\ln k_0$	E/kJ mol^{-1}	Experimental conditions	Ref.
$(CH_3)_3Al$	571–607	36.63	188.3	Static system	15
$(C_2H_5)_3Al$	435–465	18.88	121.3	"	21
$(CH_3)_3Ga$	686–983	35.7	249	Flow system, toluene carrier	23
	683–703	29.3	184	Flow system, hydrogen atmosphere	25
$(C_2H_5)_3Ga$	610–749	36.1	197.5	Flow system, toluene carrier	49
	543–1023	18.2	95	Flow system, hydrogen atmosphere	24
	573–653	11.3	95.8	Static system	27
$(n\text{-}C_3H_7)_3Ga$	473–553	13.1	76.5	"	27
$(n\text{-}C_4H_9)_3Ga$	473–553	5.8	49.8	"	27
$(CH_3)_3In$	550–781	36.2	197.5	Flow system, toluene carrier	44
$(C_2H_5)_3In$	453–523	28.3	144	Static system	42
$(n\text{-}C_4H_9)_3In$	473–553	17.7	110.8	"	43
$(n\text{-}C_5H_{11})_3In$	473–553	14.5	86.2	"	43
$(n\text{-}C_6H_{13})_3In$	473–553	13.8	63.2	"	43
$(CH_3)_3Tl$	452–536	34.7	152.3	Flow system, toluene carrier	48

Note. The parameters of the Arrhenius equation which correspond to a first-order rate constant are quoted with the exception of the parameters for $(CH_3)_3Al$, the order of the reaction of which is 3/2 and the dimensions of k are s^{-1} $mol^{-0.5}$ $litre^{0.5}$.

The enthalpy of reaction (19) is 113 ± 4 kJ mol^{-1}, which virtually agrees with the activation energy for this process and is close to the Al–N bond dissociation energy. The constant k_2 is the effective rate constant for the decomposition of AlH_3 in the gas phase.

The mechanism of the growth of a thin aluminium film on the crystalline surface of aluminium (111) has been investigated by a method involving the decomposition of the complexes of aluminium hydride with trimethylamine[52] and triethylamine.[57] The process occurring on the surface can be represented in a simplified form by the following reactions:

$$AlH_3 \cdot NR_3\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AlH_3 \cdot NR_3\,(s), \quad (23)$$

$$AlH_3 \cdot NR_3\,(s) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AlH_3\,(s) + NR_3\,(s), \quad (24)$$

$$AlH_3\,(s) \xrightarrow{k_3} Al\,(s) + 3H\,(s), \quad (25)$$

$$NR_3\,(s) \xrightarrow{k_4} NR_3\,(g), \quad (26)$$

$$3H\,(s) \xrightarrow{k_5} \tfrac{3}{2}H\,(g, s). \quad (27)$$

It was shown[52] that reaction (24)—the dissociation of the Al–N bond in the complex adsorbed on the surface—is the rate-limiting stage in the deposition of the aluminium film in the aluminium hydride–trimethylamine system, while in the aluminium hydride–triethylamine system the rate-limiting stage in the growth of the film is reaction (27)—the desorption of hydrogen atoms from the surface.[57] The activation energy for bond dissociation in $AlH_3 \cdot N(C_2H_5)_3$ on the surface has been estimated as 65–80 kJ mol^{-1}, which is less than the activation energy for the desorption of hydrogen from the surface. Epitaxial aluminium layers without an admixture of carbon were obtained at 310 K and above.[52,57]

The complexes between aluminium hydride and tertiary amines, such as $AlH_3 \cdot N(C_2H_5)_3$, $AlH_3 \cdot N(n\text{-}C_3H_7)_3$, and $AlH_3 \cdot N(n\text{-}C_4H_9)_3$, are liquids at room temperature, but their thermal stability diminishes with increase in the bulk of the substituents in the amine. Among the liquid aluminium hydride complexes, the most stable is that with ethyldimethylamine,[54] which has been used to obtain ultrapure aluminium in the construction of lasers. It has been suggested that the adduct decomposes via reactions (23)–(27).[54]

The gallium complexes $GaH_3 \cdot NR_3$ are hardly used in the formation of epitaxial layers, since, for example, $GaH_3 \cdot N(CH_3)_3$ is unstable and decomposes even at room temperature. The more stable adduct $GaH_3 \cdot NH(CH_3)_2$ has been described. It has been used in combination with AlH_3 and *tert*-$C_4H_9AsH_2$ for the formation of (AlGa)As/GaAs heterostructures.[58]

The adduct $(CH_3)_3In \cdot N(CH_3)_3$ has been synthesised in a satisfactory yield and with adequate purity from metallic indium, NMe_3, and methyl iodide in the presence of magnesium and diethyl ether.[59] The vapour pressure of the adduct was determined: 7.42 × 10^6 Pa at 323 K and 0.97 × 10^6 Pa at 293 K. For comparison, we may note that the vapour pressure of $(CH_3)_3In$ at 293 K is 1.41 × 10^6 Pa. The complex $(CH_3)_3In \cdot N(CH_3)_3$ and PH_3 have been used to prepare InP films.

III. Kinetics of the thermal decomposition of alkyl derivatives of Group V elements

The rate of thermal decomposition of gaseous alkyl derivatives of Group V elements is described by the equation for a first-order reaction regardless of the nature of the heteroatom or the alkyl group R in R_3E^V, where E^V = P, As, Sb, or Bi and R = CH_3, C_2H_5, or n-C_3H_7 (Table 2).

The kinetic parameters of the thermal decomposition of $(CH_3)_3As$ have been published[60–62] for both dynamic and static conditions. The decomposition in a closed quartz reactor[60] at 673–733 K leads to the formation of methane (~90 vol.%), ethane (4%), ethene (2.5%), hydrogen (1%), and higher hydrocarbons. Approximately the same proportions of the gaseous products have been observed in a flow reactor.[61] The solid phase contains 98.4% of metallic arsenic. An increase in the length of the hydrocarbon group diminishes the thermal stability of alkylarsines.[62,63] The reactivities of trialkylarsines increase in the sequence $(CH_3)_3As < (C_2H_5)_3As < (n\text{-}C_3H_7)_3As$. Thus, at 679 K the rate constants for the decomposition of trimethyl-, triethyl- and tri-n-propyl-arsines are 9 × 10^{-5}, 193 × 10^{-5}, and 257 × 10^{-5} s^{-1} respectively. The composition of the gaseous products indicates an increase in the contribution of the β-elimination to the overall process on passing from the ethyl to the propyl derivatives.

Systematic studies of the influence of the central heteroatom on the rate of thermal decomposition of the methyl[61,64–66] and ethyl,[62,67–70] derivatives of Group V elements showed that the reactivities of $(CH_3)_3E^V$ and $(C_2H_5)_3E^V$ increase from phosphorus to bismuth: P < As < Sb < Bi.

Comparison of the temperatures at which the effective rate constants for the pyrolysis of the ethyl derivatives of Group V elements are the same and equal to 10^{-5} s^{-1} shows that this temperature is 653 K for $(C_2H_5)_3P$, whereas the significantly lower temperature of 433 K corresponds to $(C_2H_5)_3Bi$.[67,69–71]

The composition of the products of the decomposition reaction (Table 3) indicates a radical mechanism for the decomposition of $(CH_3)_3E^V$ and the occurrence of the competing radical and molecular reactions of the corresponding ethyl derivatives $(C_2H_5)_3E^V$. Unsaturated compounds are formed via the β-elimination reactions and also as a result of the disproportionation of the alkyl radicals.

Table 2. Kinetic parameters of the decomposition of the alkyl derivatives of Group V elements.

Compound	T/K	$\ln k_0$	E/kJ mol^{-1}	Experimental conditions	Ref.
$(C_2H_5)_3P$	693–753	34.7	251.8	Static system	69, 70
	850–1050	36.8	263.6	Flow system	71
$(CH_3)_3As$	673–733	29.4	228.4	Static system	60
	764–858	36.4	262.8	Flow system, toluene carrier	61
	687–736	33.1	240	Static system	62
$(C_2H_5)_3As$	653–693	31.1	210.8	"	62, 67
	650–690	29.9	167.3	"	64
$(n\text{-}C_3H_7)_3As$	661–693	30.2	204	"	63
$(CH_3)_3Sb$	705–767	35.2	233.8	Flow system, toluene carrier	65
$(C_2H_5)_3Sb$	578–613	31.1	189.5	Static system	67
$(CH_3)_3Bi$	655–680	32.2	184	Flow system, toluene carrier	66
$(C_2H_5)_3Bi$	465–497	19.6	110.8	Static system	67

Table 3. Composition of the gaseous products of the decomposition of the methyl and ethyl derivatives of Group V elements.[62,67]

Compound	T/K	Composition (mol.%)								
		H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8	Unidentified compounds
$(CH_3)_3As$	688–731	0.4–0.27	88.1–90.4	4.9–1.5	1.1	1.9–3.5	3.6–1.3	–	–	–
$(C_2H_5)_3As$	642–693	–	5.1	77.0	8.4	2.5	5.0	2.0	–	–
$(C_2H_5)_3Sb$	578–613	–	0.5	65.3	3.3	1.9	4.0	16.4	8.3	0.7
$(C_2H_5)_3Bi$	465–497	–	–	45.5	7.3	–	–	28.8	6.3	12.0

The consecutive-parallel thermal decomposition reactions of the ethyl derivatives of Group V elements can be represented in the following way in a general form (Scheme 3):

Scheme 3

$$(C_2H_5)_3E \longrightarrow \begin{cases} (C_2H_5)_2\dot{E} + CH_3\dot{C}H_2, \\ (C_2H_5)_2EH + C_2H_4, \end{cases}$$

$$(C_2H_5)_2\dot{E} \longrightarrow C_2H_5E: + CH_3\dot{C}H_2,$$

$$(C_2H_5)_2EH \longrightarrow C_2H_5E: + C_2H_6,$$

$$C_2H_5E: \longrightarrow E + CH_3\dot{C}H_2,$$

$$2CH_3\dot{C}H_2 \longrightarrow \begin{cases} C_2H_6 + C_2H_4, \\ C_4H_{10}. \end{cases}$$

The decomposition mechanism was devised on the basis of the analysis of the composition of the stable gaseous products and does not provide, for example, for the successive transformation of $(C_2H_5)_3E^V$ into E^VH_3, because molecular hydrogen, the formation of which would have been expected in the pyrolysis of E^VH_3, is not detected in the products at fairly low temperatures. At high temperatures, the role of secondary processes involving the reactions of the ethyl radicals increases. This is the reason for the presence of methane and higher hydrocarbons in the products of the thermal decomposition of $(C_2H_5)_3As$ and $(C_2H_5)_3Sb$.[72]

The radical reactions in the pyrolysis of $(C_2H_5)_3As$ and $(C_2H_5)_2AsH$ in a stream of hydrogen and deuterium have been investigated in detail by the mass-spectrometric method.[73] Tetraethylhydrazine was used as the source of ethyl radicals. Ethyl radicals accelerated the pyrolysis of $(C_2H_5)_2AsH$ but did not affect the pyrolysis of $(C_2H_5)_3As$. Isotopic analysis of the reaction products showed that β-elimination hardly occurs in the pyrolysis of these compounds under the conditions of the given experiment and that the radical reactions predominate. It has been established by computer modelling that the proposed reaction mechanism is consistent with experimental data.

Since the hydrides of Group V elements (PH_3, AsH_3, SbH_3) are toxic, it has been suggested in recent years that somewhat less toxic compounds such as *tert*-$C_4H_9PH_2$ or *tert*-$C_4H_9AsH_2$ be used for the MOCVD processes.[74–76]

The mechanisms of the thermal decomposition of *tert*-$C_4H_9PH_2$ and *tert*-$C_4H_9AsH_2$ have been discussed.[77–83] It was shown that the molecular processes leading to the formation of $\dot{A}sH_2$ and isobutane should be regarded as dominant in the decomposition of *tert*-$C_4H_9AsH_2$ in a D_2 atmosphere when the gas phase comes into contact with a SiO_2 or GaP surface.[78] β-Elimination, accompanied by the formation of AsH_3 and isobutene, becomes appreciable at high temperatures.

In contrast to *tert*-$C_4H_9AsH_2$, the decomposition of *tert*-$C_4H_9PH_2$ is a multistage process where free-radical reactions predominate according to Li and coworkers[81,82] and Fan et al.[83]

$$tert\text{-}C_4H_9PH_2 \longrightarrow (CH_3)_3\dot{C} + H_2\dot{P} \quad (28)$$

$$tert\text{-}C_4H_9PH_2 + (CH_3)_3\dot{C} \longrightarrow (CH_3)_3CH + tert\text{-}C_4H_9\dot{P}H \quad (29)$$

$$tert\text{-}C_4H_9\dot{P}H \longrightarrow (CH_3)_3\dot{C} + HP: \quad (30)$$

$$(CH_3)_3\dot{C} \longrightarrow (CH_3)_2C{=}CH_2 + \dot{H} \quad (31)$$

The *tert*-butyl radicals are destroyed by reactions (29) and (31), while the :PH and $\dot{P}H_2$ radicals are adsorbed on the surface and interact with one another. A change in the SiO_2 surface area does not influence significantly the rate of thermal decomposition of *tert*-$C_4H_9PH_2$, whereas the GaP surface has a catalytic effect on the decomposition of phosphine.[81] Gallium atoms play the role of catalytic centres. The adsorbed species located on the neighbouring Ga atoms participate in the reaction

$$tert\text{-}C_4H_9PH_2\,(s) + PH\,(s) \longrightarrow \quad (32)$$

$$\longrightarrow (CH_3)_3CH\,(g) + PH_{x-1}\,(s) + PH_2\,(s);$$

$x = 1–2$.

At high temperatures, the intramolecular β-elimination reaction cannot be ruled out for *tert*-$C_4H_9PH_2$.[83]

$$tert\text{-}C_4H_9PH_2 \longrightarrow (CH_3)_2C{=}CH_2 + PH_3 \quad (33)$$

In contrast to *tert*-$C_4H_9PH_2$, PH_3 decomposes under the conditions of the MOCVD process at temperatures higher by ~300 °C. The mechanism of the pyrolysis of PH_3 on the surface includes the following reactions:[84]

$$PH_3\,(g) \rightleftharpoons PH_3\,(s) \quad (34)$$

$$PH_3\,(s) \rightleftharpoons PH\,(s) + H_2\,(s) \quad (35)$$

$$2PH\,(s) \longrightarrow P_2\,(s) + H_2\,(g) \quad (36)$$

$$PH_3\,(s) + PH\,(s) \longrightarrow P_2\,(s) + 2H_2\,(g) \quad (37)$$

$$2P_2\,(s) \longrightarrow 2P_2\,(g) \quad (38)$$

$$PH_3\,(s) + PH\,(s) \longrightarrow 2PH_2\,(s) \quad (39)$$

Comparison of the mechanisms of the decomposition of *tert*-$C_4H_9PH_2$ and PH_3 shows that the reactions of the radicals: PH and $\dot{P}H_2$, which generally occur on the surface, are common to them. The difference is determined by the nature of the rate-limiting stages for the processes: reaction (28) or (32) is such a stage for *tert*-$C_4H_9PH_2$, while for PH_3 it is reaction (35), which can occur both homogeneously and heterogeneously.

The study of the kinetics of the thermal decomposition of *tert*-$C_4H_9PH_2$ (22 experiments)[85] showed that the reaction is pseudo-first-order with respect to the substrate. The kinetic parameters of the pyrolytic reaction were determined in the temperature range 593–626 K at an initial pressure $P_0 = (2.2 - 2.7) \times 10^4$ Pa. The rate constant varies from 2.39 [2.39×10^{-4}? (translator)] to 12.5×10^{-4} s^{-1} and the process activation energy is 159 ± 5 kJ mol^{-1}. The composition of the gaseous decomposition products (in mol.%), determined by gas–liquid chromatography, is as follows: CH_4 (0.2), iso-C_4H_{10} (99.3), and iso-C_4H_8 (0.5). At temperatures above 780 K, the gaseous products of the

hydrolysis of *tert*-$C_4H_9PH_2$ undergo further decomposition.[85] According to the data of Li et al.,[81] further decomposition does not occur in a flow system in a D_2 atmosphere. Under static conditions in the temperature range 780–840 K, the thermal decomposition of isobutane takes place at an appreciable rate with formation of CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, and iso-C_4H_8.

The high pyrolysis temperature and the toxicity of the hydrides of Group V elements forced investigators to turn to the alkyl derivatives of Group V elements capable of generating hydrides at fairly low temperatures directly in the hot zone of the reactor. The possibility of using the compounds $As(R_r)(R_\beta)_{3-n}$ for the preparation of semiconducting layers, where R_r is the alkyl group participating in the free-radical decomposition at the $As-R_r$ bond, and R_β is the alkyl group (usually iso-C_3H_7 or *tert*-C_4H_9) undergoing β-elimination with formation of $As(R_r)_nH_{3-n}$, has been analysed.[86] A model compound of this kind is *tert*-$C_4H_9(C_2H_5)_2As$.[86] The decomposition of this compound in the temperature range 373–725 K was investigated by the mass-spectrometric method. It was established that at 373–573 K the free-radical decomposition of this compound predominates over β-elimination (in proportions of 2:1). At a temperature above 620 K, β-elimination is the main process leading to the formation of $(C_2H_5)_2AsH$.

$$\textit{tert}\text{-}C_4H_9(C_2H_5)_2As \longrightarrow (C_2H_5)_2AsH + \text{iso-}C_4H_8$$

The hydride $(C_2H_5)_2AsH$ is a source of arsenic in the preparation of epitaxial III–V layers.

Similarly it has been suggested that *tert*-$C_4H_9(CH_3)_2Sb$ be employed to prepare InSb layers. The temperature at which the epitaxial layers are grown is then reduced by about 100 °C compared with the process employing $(CH_3)_3Sb$ and by about 50 °C compared with (iso-$C_3H_7)_3Sb$.[87,88]

Comparison of the reactivities of alkyl derivatives of Group III and V elements (Tables 1 and 2) indicates a higher thermal stability of $(CH_3)_3E^V$ compared with $(CH_3)_3E^{III}$ (E^{III} and E^V are Group III and V elements in the same Period). Price and coworkers[23,44,48,49,61,65,66] carried out systematic studies on the kinetics of the thermal decomposition of the methyl derivatives of the above elements in a flow system, using toluene as the carrier gas. We used these data to compare the reactivities of the alkyl derivatives of Group III and V elements. The linear plots of $\ln k_{R_3E^{III}}$ against $\ln k_{R_3E^V}$ presented in Fig. 1 (lines *1* and *2*) confirm the existence of a correlation between the rate constants for the pyrolysis of the methyl derivatives of Group III elements and the rate constants for the pyrolysis of the methyl derivatives (line *1*) and ethyl derivatives (line *2*) of Group V elements. This finding confirms that the mechanisms of the pyrolysis of the compounds R_3E of Group III and V elements are of the same type. A certain scatter of the points about line *1* is associated with the fact that constants obtained by extrapolation were compared. The relations presented permit an estimate of the rate constant for the thermal decomposition of the monomeric compound $(CH_3)_3Al$, which proved to be 10^{-8} s^{-1} at 688 K. Hence it follows that the monomeric trimethylaluminium is a very stable compound. The rate constant for the pyrolysis of $(CH_3)_3Al$ obtained experimentally[15] at this temperature proved to be significantly higher than the value quoted. This is associated with the fact that the kinetically active species in the thermolysis is the dimer, its presence in the vapour phase reducing the thermal stability of the monomer in equilibrium with it.

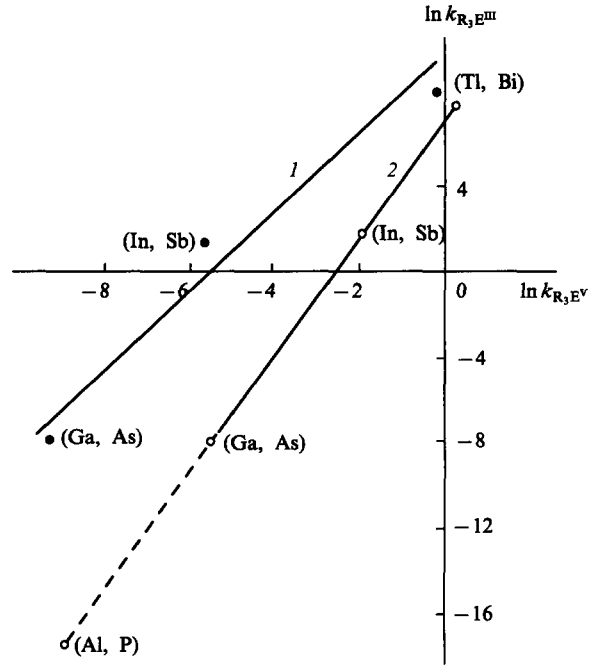


Figure 1. Relation between the rate constants for the pyrolysis of the methyl derivatives of Group III elements and the rate constants for the pyrolysis of the methyl (line *1*) and ethyl (line *2*) derivatives of Group V elements ($T = 488$ K).

IV. Joint decomposition of the organoelement compounds and hydrides of Group III and V elements in the gas phase and under the conditions for the formation of epitaxial layers

It follows from the data presented in Tables 1 and 2 that the majority of organometallic alkyl derivatives of Group III elements decompose in the temperature range 450–650 K, whereas the analogous compounds of Group V elements decompose at higher temperatures (600–850 K). The 'gap' between the temperature ranges of the decomposition reactions complicates the preparation of high-quality epitaxial III–V layers and heterostructures. As a rule, it is necessary to introduce the Group V compound into the reaction system in a large excess (by a factor of 10–100). However, the 'gap' is only apparent, since during their joint decomposition the compounds of Group III and V elements influence one another and the difference between their thermal stabilities is eliminated. The change in thermal stability may be associated with the possibility of the formation of adducts between the mixture components.

$$R_3M^{III} + R_3E^V = R_3M^{III} \cdot E^VR_3$$

The formation of such complexes follows from the acid–base properties of the reactants, since the organoelement compounds of Group III elements, having an unoccupied orbital, behave as Lewis acids, while the compounds of Group V elements, containing a lone pair, behave as Lewis bases.

The formation of adducts promotes the polarisation of the M–C bonds and changes in the steric configuration of the molecules, in the interatomic distances, and in the bond angles.[89] For example, the study of the NMR spectra of $(C_2H_5)_3Al$, $(C_2H_5)_3Ga$, and their etherates led to the conclusion that the element–carbon bonds in the complexes with ether are 'loosened' to a greater extent than the E–C bonds in the initial alkyl complexes.[90]

In the series of alkyl derivatives of Group V elements, the electron-donating properties are weakened in the following

sequence: N > P > As > Sb > Bi.[91-93] Among the compounds of Group III elements, the most pronounced electron-accepting properties are those of R_3Al.[91]

The thermal stability of the mixture of organoelement compounds is determined by the stabilities of kinetically independent species of different types: the molecules of individual compounds, their adducts, dimers, and the intermediates of the decomposition reaction formed in the mixture. The alkyl derivatives of Group III and V elements are known[91] to form fairly stable complexes $R_3M^{III}.E^VR_3$. The possibility of the existence of these complexes under the conditions of the thermal decomposition of the $(CH_3)_3Ga + (CH_3)_3As$ and $(CH_3)_3Al + (CH_3)_3As$ mixtures has been investigated.[94-97] The vapour pressure of the complex $(CH_3)_3Ga \cdot As(CH_3)_3$ was investigated at different temperatures and it was shown that the complex is fully dissociated in the gas phase at 470 K.[94] Under the severe conditions of the thermal decomposition of $(CH_3)_3Ga$ and $(CH_3)_3As$, one can therefore consider only the probability of the existence of the adduct $(CH_3)_3Ga \cdot As(CH_3)_3$,[96] which could not be detected with the aid of Raman spectroscopy.[98]

The rates and mechanisms of the thermochemical, photochemical, and plasmochemical decomposition of the mixture of organoelement compounds depend on the contribution by the decomposition of the complex to the effective pyrolysis rate constant. Thus, when $(CH_3)_3Ga$ and $(CH_3)_3As$ are mixed, the rate of their joint thermal decomposition increases by a factor of ~1.5–2 compared with the individual organoelement compounds.[95] Therefore knowledge of the thermodynamic and kinetic characteristics of the complexes formed becomes useful for the understanding of the kinetics of the joint decomposition of the organoelement compounds. The complexes $(CH_3)_3E \cdot As(CH_3)_3$ (E = Al, Ga, In) were synthesised in vacuo (P = 1–2 Pa) by mixing the initial organoelement compounds. $(CH_3)_3As$ was taken in excess and was then removed from the reactor by freezing out in a trap cooled with liquid nitrogen. By repeated sublimation, the complexes may be freed from the possible impurities comprising the individual organoelement compounds. The melting points (T_m) of the complexes $(CH_3)_3E \cdot As(CH_3)_3$ are given below.

E	T_m/K	Ref.
Al	304.2	96
Ga	296.6	91
	296.4–296.7	91
In	297.6	96
	297.2–297.8	91

The change in the Gibbs free energy or the dissociation constant K_e serves as a measure of the thermal dissociation of the complexes. The capacity of the test complexes[96,97] for thermal dissociation increases in the sequence

$$(CH_3)_3Al \cdot As(CH_3)_3 < (CH_3)_3In \cdot As(CH_3)_3 < (CH_3)_3Ga \cdot As(CH_3)_3.$$

For example, at 430 K the dissociation constants K_e for the above series of compounds are respectively 0.21, 1.005, and 3.51 atm.[97]

The temperature dependence of K_e suggests that the concentrations of the complexes are very low in the processes involving the high-temperature (~800 K) deposition of epitaxial layers. However, one cannot rule out the possibility that the role of such complexes in the kinetics of the pyrolysis is the same as that of free radicals and other active intermediate species. At lower temperatures (~350 K), the saturated vapour is a mixture of the gaseous complex and its dissociation products. The degree of dissociation of the complexes in equilibrium with the liquid phase at any temperature can be readily determined from K_e and the pressure P.

The rate of thermal decomposition of a mixture of $(CH_3)_3Al$ and $(CH_3)_3As$ has been investigated and the kinetic data obtained have been compared with the results for the thermal decomposition of the individual aluminium and arsenic compounds.[96] When gaseous $(CH_3)_3Al$ and $(CH_3)_3As$ are mixed at room temperature, the crystalline complex $(CH_3)_3Al \cdot As(CH_3)_3$ is formed. It was established that the arsine decomposes in the mixture independently of $(CH_3)_3Al$. On the other hand, the presence of $(CH_3)_3As$ influences the nature of the thermal decomposition of $(CH_3)_3Al$: firstly, its thermal stability increases (the temperature range of the decomposition reaction shifts from 590–650 K to 670–720 K) and, secondly, its decomposition is described by the kinetic equation for a first-order reaction. The results led to the following hypothesis concerning the mechanism of the joint decomposition of the above organoelement compounds: at 420–470 K, the saturated vapour obtained on evaporation of the complex $(CH_3)_3Al \cdot As(CH_3)_3$ is an equilibrium mixture of the individual OEC, the complex, and dimeric trimethylaluminium.

$$(CH_3)_3Al \cdot As(CH_3)_3 \rightleftharpoons (CH_3)_3Al + (CH_3)_3As$$
$$\Downarrow\Uparrow$$
$$[(CH_3)_3Al]_2$$

With increase in temperature, the complex and the dimer dissociate. Under the conditions of the thermal decomposition (670–720 K), the equilibrium concentrations of the dimer and the complex become insignificant. This may be inferred from results on the thermodynamic measurements of the degree of dissociation of dimeric trimethylaluminium.[18] However, even small amounts of the dimer and the complex may prove to be kinetically active in the thermal decomposition process. Therefore, under the pyrolysis conditions, it is essential to take into account the following paths in the reaction of the OEC:

$$\dot{C}H_3 + (CH_3)_2\dot{A}l + As(CH_3)_3 \qquad \dot{C}H_3 + (CH_3)_2\dot{A}s$$
$$\uparrow k_1' \qquad \uparrow k_2$$
$$(CH_3)_3Al \cdot As(CH_3)_3 \rightleftharpoons (CH_3)_3Al + As(CH_3)_3$$
$$\swarrow\!\!\swarrow \qquad \searrow k_1''$$
$$[(CH_3)_2Al]_2 \qquad \dot{C}H_3 + (CH_3)_2\dot{A}l$$
$$\downarrow k_1'''$$
$$2\dot{C}H_3 + \text{polymer}.$$

The experimentally determined constant k_1 (see below) is an effective quantity and includes the constants for the primary elementary stages k_1', k_1'', and k_1'''.

The Arrhenius relations for the temperature variation of the rate constants for the decomposition of $(CH_3)_3Al$ and $(CH_3)_3As$ in the mixture can be represented by the equations

$$\ln k_1 = (14.8 \pm 4.4) - \frac{123 \pm 10}{RT} \quad \text{for } (CH_3)_3Al,$$

$$\ln k_2 = (33.1 \pm 1.5) - \frac{240 \pm 9}{RT} \quad \text{for } (CH_3)_3As.$$

The formation of a 1 : 1 adduct of trimethylgallium and arsine has been demonstrated by the matrix isolation method in an argon matrix at 77 K.[99] Its spectroscopic characteristics have been published. The thermal stability of $(CH_3)_3Ga$ decreases on mixing with the arsine. The decomposition is observed already at 476 K.[92] The degree of decomposition increases with increase in temperature.[100]

$$Me_3Ga \cdot AsH_3 \longrightarrow Me_2Ga{-}AsH_2 + CH_4$$
$$Me_2Ga{-}AsH_2 \longrightarrow \text{-[MeGa-AsH]-}_n + CH_4$$
$$\text{-[MeGa-AsH]-}_n \longrightarrow GaAs + CH_4$$

The indium-containing adducts $R_3In \cdot AsH_3$, which are formed even at room temperature, are still more reactive.[101,102]

The formation of the adducts $R_3M^{III} \cdot E^V R'_3$ or the dimers $(R_3M)_2$ must be taken into account in describing the kinetics and mechanism of their decomposition. They influence significantly the mass transfer conditions in the chemical gas-phase deposition. The rate of thermal decomposition of arsine[26,104,106] increases significantly in the presence of $(CH_3)_3Ga$ and arsine itself reduces the thermal stability of $(C_2H_5)_3Ga$.[100,106-108]

An important factor in the variation of the thermal stability of the mixture of OMC is the exchange interaction between them. The exchange of radicals between $(CH_3)_3Ga$ and $(CH_3)_3Al$ [109] and also between $(iso\text{-}C_4H_9)_3Al$ and $(CH_3)_3Al$ [110] has been established by NMR spectroscopy. Such exchange alters the reactivities of the mixture components as a consequence of the change in the composition of the OEC.

The pyrolysis of $(C_2H_5)_3Ga$ in the presence of AsH_3 and $(CH_3)_3Al$ in a stream of H_2 has been investigated mass-spectrometrically.[107] It was established that the decomposition of $(C_2H_5)_3Ga$ is influenced by the components of the gas mixture: arsine diminishes the temperature of the pyrolysis of $(C_2H_5)_3Ga$ approximately by 20 °C, while $(CH_3)_3Al$ increases it by 25 °C. This is associated with the different mechanisms of the decomposition of $(C_2H_5)_3Ga$ in the presence of the above components. The rate-limiting stages of the processes differ significantly.

In a mixture of $(C_2H_5)_3Ga$ and AsH_3 in a stream of hydrogen, the main reactions are

$$(C_2H_5)_3Ga \longrightarrow CH_3\dot{C}H_2 + (C_2H_5)_2\dot{G}a,$$
$$CH_3\dot{C}H_2 + AsH_3 \longrightarrow C_2H_6 + \dot{A}sH_2,$$
$$CH_3\dot{C}H_2 + \dot{A}sH_2 \longrightarrow C_2H_5AsH_2,$$

while in a mixture of $(C_2H_5)_3Ga$ and $(CH_3)_3Al$ exchange reactions take place and mixed alkyl derivatives are formed.

$$2(CH_3)_3Al \rightleftharpoons (CH_3)_2Al(\mu\text{-}CH_3)_2Al(CH_3)_2$$

$$(C_2H_5)_3Ga + (CH_3)_2Al(\mu\text{-}CH_3)_2Al(CH_3)_2 \rightleftharpoons \quad (40)$$

$$\rightleftharpoons (CH_3)_2Al(\mu\text{-}CH_3)(\mu\text{-}C_2H_5)Ga(C_2H_5)_2 + (CH_3)_3Al$$

$$\Downarrow$$

$$(CH_3)_2C_2H_5Al + CH_3(C_2H_5)_2Ga$$

$$(CH_3)_3Al + CH_3(C_2H_5)_2Ga \longrightarrow \quad (41)$$
$$\longrightarrow (CH_3)_2C_2H_5Al + (CH_3)_2C_2H_5Ga$$

The compounds $CH_3(C_2H_5)_2Ga$ and $(CH_3)_2C_2H_5Ga$ formed in the exchange reactions (40) and (41) are thermally more stable than $(C_2H_5)_3Ga$. This explains the increase in the temperature of the pyrolysis of the mixture of $(C_2H_5)_3Ga$, $(CH_3)_3Al$, and H_2. As a result of the occurrence of the equilibrium reactions (40) and (41), the pyrolysis is undergone virtually not by the two individual OEC but by a mixture with a complex chemical composition.

It has been noted that the bimolecular reaction between $(CH_3)_3Ga$ and arsine alters the thermal stability of this mixture.[111-114]

Direct measurements of the concentration of the methyl radicals by means of laser IR spectroscopy made it possible to estimate the relative contributions of certain reactions to the joint decomposition of AsH_3 with $(CH_3)_3Ga$ or $(CH_3)_3In$ in a hydrogen atmosphere.[115]

$$\dot{C}H_3 + H_2 \longrightarrow CH_4 + \dot{H} \quad (42)$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow \begin{cases} C_2H_6 & (43) \\ CH_4 + {:}CH_2 & (44) \\ C_2H_4 + H_2 & (45) \end{cases}$$

$$\dot{C}H_3 + AsH_m \longrightarrow CH_4 + \dot{A}sH_{m-1} \quad (46)$$

$$\dot{C}H_3 + (CH_3)_nM \longrightarrow \begin{cases} CH_4 + (CH_3)_{n-1}M\dot{C}H_2 & (47) \\ C_2H_6 + (CH_3)_{n-1}\dot{M} & (48) \end{cases}$$

$$(CH_3)_nM \longrightarrow \dot{C}H_3 + (CH_3)_{n-1}\dot{M} \quad (49)$$

$$(CH_3)_nM + AsH_m \longrightarrow (CH_3)_nM \cdot AsH_m \quad (50)$$

$n, m = 1-3$; M = Ga, In.

One cannot exclude from consideration reactions (42), (44), and (47) as potential sources of methane. The main supplier of methyl radicals in these processes is reaction (49). Reactions (43) and (48) are insignificant at low concentrations of the OEC, so that ethane is virtually absent from the reaction products. The formation of ethene has been observed only at temperatures above 870 K [reaction (45)]. The concerted variation of the concentrations of methyl radicals and methane has been noted when AsH_3 was introduced into the $(CH_3)_3M$ undergoing decomposition, which confirms the important role of reaction (46) in the chemical gas-phase deposition of epitaxial GaAs or InAs layers.

Within the framework of the classical Langmuir–Hinshelwood theory of the growth of layers, it has been possible to differentiate the kinetic and diffusional temperature ranges corresponding to the development of the MOCVD process.[116-120] For example, in a stream of hydrogen the kinetic region corresponding to the growth of the GaAs layer from $(CH_3)_3Ga$ and AsH_3 occurs in the temperature range 720–870 K. According to the results of Reep and Chandhi,[117] the effective process activation energy is 92 kJ mol^{-1}, which differs little from the activation energy for the heterogeneous decomposition of AsH_3.[108] It has been suggested that the adsorption of AsH_3 and its subsequent decomposition are the rate-limiting stages in the deposition of GaAs. The temperature range 870–1120 K corresponds to the diffusional region of the growth of the GaAs film. In this range, the rate of growth is almost independent of temperature. The apparent activation energy is only ~8.4 kJ mol^{-1}. A further increase in temperature leads to the 'etching' of the epitaxial layer.

Evidence for the formation of the intermediates CH_3AsH_2 and $(CH_3)_2AsH$ in the pyrolysis of a mixture of $(CH_3)_3Ga$ and AsH_3 and also of $C_2H_5AsH_2$ in the decomposition of $(C_2H_5)_3Ga$ in the presence of AsH_3 has been obtained by IR spectroscopy.[121] The formation of a complex between R_3Ga and AsH_3 and the surface reactions are not then taken into account, the radical gas-phase reactions being considered in detail (Scheme 4). A characteristic feature of this scheme is the hypothesis of the formation as intermediates of complexes of the alkyl radicals produced on decomposition of R_3Ga in the presence of arsenic hydrides with different degrees of substitution, i.e. $R_{4-m}\dot{A}sH_m$, where $m = 1-3$.

Scheme 4

$R_3Ga \longrightarrow \dot{R} + R_2\dot{G}a$

$R_2\dot{G}a \longrightarrow \dot{R} + RGa$

$RGa \longrightarrow \dot{R} + Ga$

$\dot{R} + AsH_3 \longrightarrow RH + \dot{A}sH_2$

$\dot{R} + \dot{A}sH_2 \longrightarrow RAsH_2$

$\dot{R} + AsH_3 \longrightarrow R\dot{A}sH_3 \longrightarrow RAsH_2 + \dot{H}$

$\dot{R} + RAsH_2 \longrightarrow RH + R\dot{A}sH$

$\dot{R} + R\dot{A}sH \longrightarrow R_2AsH$

$\dot{R} + RAsH_2 \longrightarrow R_2\dot{A}sH_2 \longrightarrow R_2AsH + \dot{H}$

$\dot{R} + R_2AsH \longrightarrow RH + R_2\dot{A}s$

$\dot{R} + R_2\dot{A}s \longrightarrow R_3As$

$\dot{R} + R_2AsH \longrightarrow R_3\dot{A}sH \longrightarrow R_3As + \dot{H}$

The decomposition of $(CH_3)_3As$ and $(C_2H_5)_3Ga$ on the GaAs surface has been investigated mass-spectrometrically.[122] The rate constant found for the decomposition of $(CH_3)_3As$ (231.5) is much higher than the values obtained in a toluene atmosphere[61] and in the absence of a carrier gas.[60] The difference is associated not only with the influence of the carrier gas and with the catalysis by the GaAs surface, but apparently also with the formation of an adduct between the mixture components. The simplified model of the decomposition process then assumes the following form:

$(C_2H_5)_3\dot{G}a \longrightarrow (C_2H_5)_{3-x}Ga + x\,CH_3\dot{C}H_2,$

$(C_2H_5)_{3-x}Ga + (CH_3)_3As \longrightarrow (C_2H_5)_{3-x}Ga\cdot As(CH_3)_3,$

$(C_2H_5)_{3-x}Ga\cdot As(CH_3)_3 \longrightarrow GaAs(CH_3)_3 + (3-x)CH_3\dot{C}H_2,$

$(C_2H_5)_3Ga + (CH_3)_3As \rightleftharpoons (C_2H_5)_3Ga\cdot As(CH_3)_3,$

$(C_2H_5)_3Ga\cdot As(CH_3)_3 \rightleftharpoons GaAs(CH_3)_3 + 3CH_3\dot{C}H_2,$

$x = 1-3.$

The kinetics and mechanism of the joint pyrolysis of $(CH_3)_3Ga$ and AsH_3 on the growing GaAs surface have been investigated at low pressures of the initial reactants (1.3×10^{-2} Pa).[31] The primary stages in this case are the adsorption of $(CH_3)_3Ga$ on the surface (on Ga or As centres) and the subsequent removal of the methyl group from the surface [reactions (51) and (52)].

$(CH_3)_3Ga\,(g) \rightleftharpoons (CH_3)_3Ga\,(s)$ (51)

$(CH_3)_3Ga\,(s) \longrightarrow (CH_3)_xGa\,(s) + (3-x)CH_3\,(s)$ (52)

$x = 0-2.$

Methyl radicals are adsorbed on the Ga and As centres and are then desorbed into the gas phase.

$CH_3E\,(s) \longrightarrow \dot{C}H_3\,(g) + E\,(s)$ (53)

E = Ga, As.

Reactions (54) and (55) reflect the different paths to the formation of ethane.

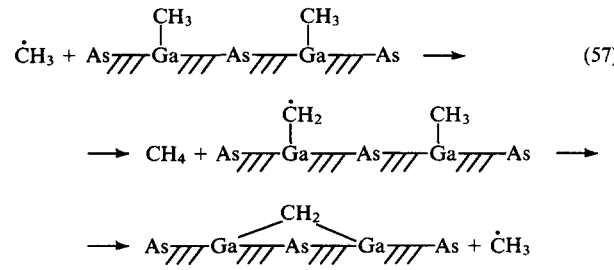
$\dot{C}H_3\,(g) + CH_3Ga\,(s) \longrightarrow C_2H_6 + Ga\,(s)$ (54)

$\dot{C}H_3\,(s) + \dot{C}H_3\,(s) \longrightarrow C_2H_6\,(g)$ (55)

The process becomes important only at temperatures above 850 K.

$(CH_3)_xGa\,(s) \rightleftharpoons (CH_3)_xGa\,(g)$ (56)

Reaction (57) demonstrates the possible ways in which carbon can be inserted in the growing epitaxial layer.



(57)

A methyl radical from the gas phase attacks the methyl group of the CH_3Ga fragment on the surface and abstracts a hydrogen atom. The resulting $\dot{C}H_2Ga$ fragment displaces a methyl radical from a neighbouring surface centre, forming a CH_2 bridge.

The products of the decomposition of AsH_3 were not detected in the gas phase (low pressure of the initial reactants). Reactions (58) and (60) reflect the AsH_3 decomposition processes on the surface.

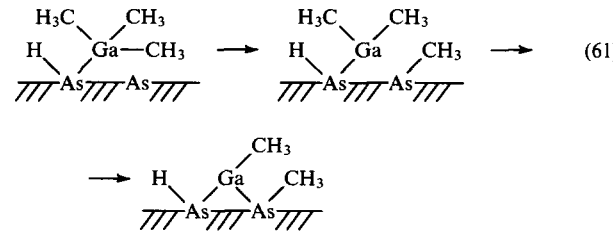
$AsH_3\,(g) \rightleftharpoons AsH_3\,(s)$ (58)

$AsH_3\,(s) \longrightarrow AsH_y\,(s) + (3-y)\dot{H}\,(s)$ (59)

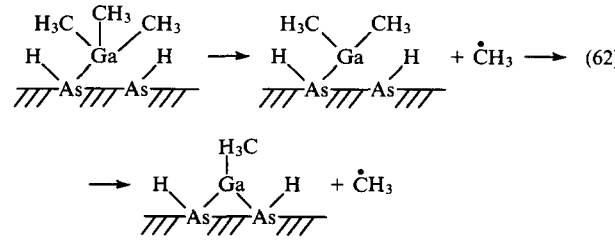
$H_yAsGa(CH_3)_x\,(s) \longrightarrow GaAs\,(s) + y\dot{H}\,(g) + x\dot{C}H_3\,(g)$ (60)

$y = 0-2.$

At low pressures of the reactants, the reactions occurring on the surface can probably be represented in the following way:



(61)



(62)

Reactions (61) and (62) correspond to the concerted processes occurring on the growing GaAs surface. The activation energy for the pyrolysis of $(CH_3)_3Ga$ on the surface is 108.8 kJ mol^{-1} and the pre-exponential factor is $10^{13.3}$ s^{-1}. The presence of arsine increases the rate of decomposition of $(CH_3)_3Ga$, whereupon E diminishes to ~84 kJ mol^{-1}.

A complex of the donor–acceptor type has been obtained in the reaction of $(CH_3)_3Ga$ with *tert*-$C_4H_9PH_2$. When the components are mixed in 1 : 1 molar proportions at room temperature, a liquid with a low vapour pressure is produced.[85]

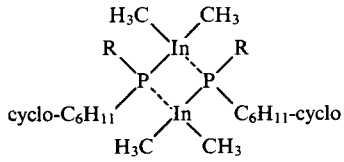
On the basis of the results of a study[81] in which it had been established that *tert*-$C_4H_9PH_2$ accelerates the decomposition of $(CH_3)_3Ga$, remaining insensitive to its presence, Yablokov et al.[85] expected to observe two different temperature ranges for the decomposition of this mixture. One should have corresponded to the decomposition of *tert*-$C_4H_9PH_2$ and the other to the

decomposition of $(CH_3)_3Ga$. In reality, the process proved to be more complex. In the temperature range 513–520 K, the rate of thermal decomposition of the mixture is described by the kinetic equation for a first order reaction and assumes the following numerical form for the rate constant (in s^{-1}):

$$\lg k = (17.2 \pm 0.8) - \frac{(125 \pm 6)}{8.314T} .$$

The mixture of gaseous decomposition products consists of CH_4 (73.4 mol.%), C_2H_6 (0.21 mol.%), iso-C_4H_{10} (17.4 mol.%), and iso-C_4H_8 (9 mol.%). This product composition differs from that in the decomposition of the individual *tert*-$C_4H_9PH_2$ (where the amount of isobutane is 99.3 mol.%) and the authors[85] therefore postulated that the complex $(CH_3)_3Ga.$*tert*-$C_4H_9PH_2$ decomposes in the temperature range 513–520 K. CH_4 and the condensation products $[(CH_3)_2Ga-PHC_4H_9$-*tert*$]$ and $[CH_3Ga-PC_4H_9$-*tert*$]_n$ are formed. Their decomposition temperature is above 680 K. The probable mechanism of the joint decomposition of *tert*-$C_4H_9PH_2$ and $(CH_3)_3Ga$ has been put forward,[85] but it requires further confirmation.

Similar phenomena have been observed on mixing *tert*-$C_4H_9PH_2$ or $C_6H_{11}PH_2$ with $(CH_3)_3In$.[83] The adduct obtained on interaction of $C_6H_{11}PH_2$ with $(CH_3)_3In$ and deposited at room temperature on the walls of the reactor and of the measuring spectroscopic cell has the following structure:



The processes involving the pyrolysis of $(CH_3)_3Ga$ and R_3As on the GaAs(001) surface have been investigated[123] by the surface photoabsorption method[124] under the conditions of the MOCVD process. In the pyrolysis of $(CH_3)_3Ga$ on the GaAs surface, the rate-determining stage in the growth of the film is the desorption of methyl radicals from the surface. In the study of the pyrolysis of $(CH_3)_3As$, $(C_2H_5)_3As$, $(C_2H_5)_2AsH$, and *tert*-$C_4H_9AsH_2$, process activation energies of 2.93, 1.58, 0.82, and 0.82 eV respectively were determined (for comparison, we may note that the activation energy for the pyrolysis of AsH_3 is 0.74 eV). The authors postulate that $(C_2H_5)_2AsH$ and *tert*-$C_4H_9AsH_2$ are possible sources of hydrogen, alternative to AsH_3, in the MOCVD processes, since the activation energy for their pyrolysis is relatively low.

Fundamental advances have been made in the modelling of processes occurring in the complex $(CH_3)_3Ga-(CH_3)_3As-AsH_3-H_2$ multicomponent system in the gas phase and on the surface of GaAs epitaxial layers.[36] The authors were interested in the mechanism of the incorporation of carbon atoms in the epitaxial layers. The proposed mechanisms of the formation of such layers include 23 gas-phase and 64 surface reactions, in which 20 gaseous compounds and 14 compounds adsorbed on the surface participate. Fig. 2 illustrates schematically the principal reaction paths of these compounds in the MOCVD process. The communication cited[36] presents the kinetic and activation parameters for all the gas-phase and surface reactions calculated from literature sources and the author's own data.

Preliminary analysis of the kinetic model showed that contamination of the epitaxial layers by carbon takes place as a result of surface reactions in which the $GaCH_3$ intermediate species is most important. The gas-phase reactions do not affect the contamination of the surface layers by carbon.

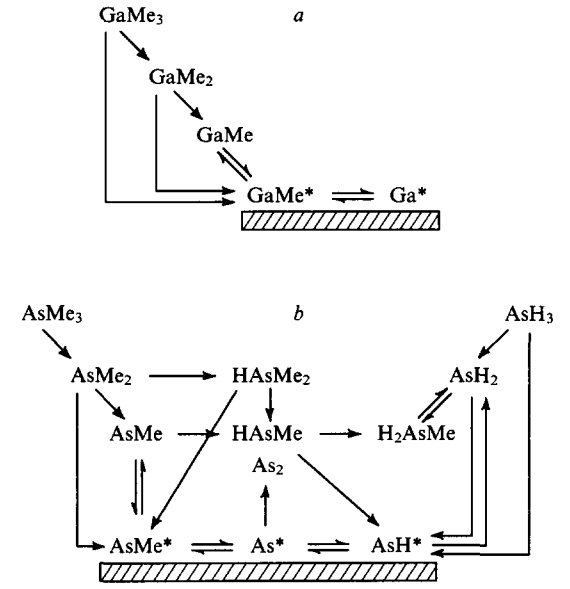


Figure 2. Schematic representation of gas-phase and surface paths of decomposition of OEC in the system $(CH_3)_3Ga-(CH_3)_3As-AsH_3$ in a stream of hydrogen (after Masi et al.[36]): (*a*) decomposition of $(CH_3)_3Ga$; (*b*) decomposition of $(CH_3)_3As$ and AsH_3.

V. Conclusion

Investigators have now come closer to understanding the detailed mechanism of the pyrolysis of the OEC of Group III and V elements in the gas phase and on the surface to such an extent that they are able to obtain excellent epitaxial layers, finding their way successfully through the labyrinth of incompatible, as regards thermal stability, explosive and toxic OEC.

The set of alternative organoelement sources in the MOCVD technology has expanded. The causes of the decrease in the rate of pyrolysis of both individual OEC and their mixtures have become understood. Ideas have been formulated concerning the combined study of the stability of OEC from the standpoint of the stability of an isolated molecule, the thermodynamic and kinetic stabilities, and also the dynamic stability of thermodynamically irreversible systems consisting of the OEC and the products of their decomposition in specific states of aggregation in the presence of mass and energy fluxes under conditions close to and remote from thermodynamic equilibrium.[125–128]

It is likely that these aspects of the investigations will in fact permit the development not only of the MOCVD technology for optoelectronics and semiconductor techniques but also for the solution of theoretical problems concerning the reactivity in the macro- and micro-processes occurring with participation of the OEC.

References

1. G B Stringfellow *J. Cryst. Growth* **115** 1 (1991)
2. M J Ludowise *J. Appl. Phys.* **58** 31 (1985)
3. K R Murali, M Jayachancran, N Rangarajan *Bull. Electrochem.* **3** 261 (1987)
4. B V Zhuk *Usp. Khim.* **54** 1312 (1985) [*Russ. Chem. Rev.* **54** 770 (1985)]
5. D W Shaw, in *Crystal Growth: Theory and Techniques* Vol. 1 (Ed. C Goodman) (London: Plenum, 1974) p. 1
6. H M Manasevit *Appl. Phys. Lett.* **12** 156 (1968)
7. H M Manasevit, W I Simpson *J. Electrochem. Soc.* **116** 1725 (1969)
8. H M Manasevit *J. Cryst. Growth* **13** 306 (1972)
9. H M Manasevit *J. Cryst. Growth* **55** 1 (1981)

10. G A Razuvaev, B G Gribov, G A Domrachev, B P Salomatin *Metalloorganicheskie Soedineniya v Elektronike* (Organometallic Compounds in Electronics) (Moscow: Nauka, 1972)
11. B G Gribov, G A Domrachev, B V Zhuk, B S Kaverin, B I Kozyrkin, V V Mel'nikov, O N Suvorova *Osazhdenie Plenok i Pokrytii Razlozheniem Metalloorganicheskikh Soedinenii* (Deposition of Films and Coatings by the Decomposition of Organometallic Compounds) (Moscow: Nauka, 1981)
12. M Suzuky, M Sato *J. Electrochem. Soc.* **132** 1684 (1985)
13. M R Leys *Chemtronics* **2** 155 (1987)
14. P W Lee, T R Omstead, D R Mckenna, K F Jensen *J. Cryst. Growth* **85** 165 (1987)
15. L M Yeddanapalli, C C Schubert *J. Chem. Phys.* **14** 1 (1946)
16. M Suzuki, C Arayma, K Mazu, K Tsubouchi, N Mikoshiba *Jpn. J. Appl. Phys.* **25** 1236 (1986)
17. V I Tel'noi, in *Tr. po Khimii i Khim. Tekhnologii* (Studies in Chemistry and Chemical Technology) (Gor'kii: Izd. Go'kovsk. Gos. Univ., 1974) No. 1, p. 28
18. A W Laubengayer, W F Gilliam *J. Am. Chem. Soc.* **63** 477 (1941)
19. D W Squire, C S Dulcey, M C Lin *Chem. Phys. Lett.* **116** 525 (1985)
20. J N Hay, P G Hooper, C Robb *J. Organomet. Chem.* **28** 193 (1971)
21. W L Smith, T Wartik *J. Inorg. Nucl. Chem.* **29** 629 (1967)
22. G B Sakharovskaya, N N Korneev, N N Smirnov, A F Popov *Zh. Obshch. Khim.* **44** 584 (1974)
23. M G Jacko, S J W Price *Can. J. Chem.* **41** 1560 (1963)
24. E P Bochkarev, L I Zakharkin, Yu V Yushkov, L S Ivanov, N P Fatyushina, V V Gavrilenko, Yu S Demen'tev, A G Petrik, V A L'vova *Nauch. Tr. Nauchno.-Issled. Proekt. Inst. Redkometal. Promsti.* **46** 6 (1973)
25. L S Ivanov, N P Fatyushina, I I Nalivaiko, V M Timashkov, S A Sadof'eva *Nauch. Tr. Nauchno.-Issled. Proekt. Inst. Redkometal. Promsti.* **112** 10 (1982)
26. S R DenBaars, B Y Maa, P D Dapkus, A D Danner, H C Lee *J. Cryst. Growth* **77** 188 (1986)
27. Yu A Aleksandrov, G I Makin, O N Druzhkov, Yu Yu Baryshnikov, T K Postnikova, B I Kozyrkin *Zh. Obshch. Khim.* **51** 70 (1981)
28. T J Mountziaris, K F Jensen *J. Electrochem. Soc.* **138** 2426 (1991)
29. C A Larsen, N I Buchan, S H Li, G B Stringfellow *J. Cryst. Growth* **102** 103 (1990)
30. Q Chen, P D Dapkus *J. Electrochem. Soc.* **138** 2821 (1991)
31. J T Francis, C W Benson, T T Tsotsis *J. Cryst. Growth* **112** 474 (1991)
32. X Y Zhu, J M White, J R Creighton *J. Vac. Sci. Technol. A, Vac. Surf. Films* **10** 316 (1992)
33. H A Skinner *Adv. Organomet. Chem.* **2** 49 (1964)
34. S J C Irvine, J B Mullin *J. Cryst. Growth* **79** 371 (1986)
35. J Haigh, S O'Brien *J. Cryst. Growth* **67** 75 (1984)
36. M Masi, H Simka, K F Jensen, T F Kuech, R Potemski *J. Cryst. Growth* **124** 483 (1992)
37. M L Yu, U Memmert, N I Buchan, T F Kuech *Mater. Res. Soc. Symp. Proc.* **222** 3 (1991)
38. J R Creighton, B A Banse *Mater. Res. Soc. Symp. Proc.* **222** 15 (1991)
39. J Kawai, H Ito, K Hara *J. Cryst. Growth* **115** 216 (1991)
40. V N Kondrat'ev, E E Nikitin, A I Reznikov, S Ya Umanskii *Khimicheskie Bimolekulyarnye Reaktsii v Gazakh* (Chemical Bimolecular Reactions in Gases) (Moscow: Nauka, 1976)
41. M Tsuda, S Oikawa, M Morishita, M Mashita *Jpn. J. Appl. Phys.* **26** 564 (1987)
42. N S Lokhov, A D Zorin, A V Tomadze, T V Kuznetsova, V F Zanozina, V A Yablokov *Zh. Obshch. Khim.* **49** 1921 (1979)
43. Yu A Aleksandrov, O N Druzhkov, Yu Yu Baryshnikov, T K Postnikova, T I Makin, B I Kozyrkin *Zh. Obshch. Khim.* **50** 2642 (1980)
44. M G Jacko, S J W Price *Can. J. Chem.* **42** 1198 (1964)
45. N I Buchan, C A Larsen, G B Stringfellow *J. Cryst. Growth* **92** 591 (1988)
46. K L Fry, C P Kuo, C A Larsen, R M Cohen, G B Stringfellow, A Melas *J. Electron. Mater.* **15** 91 (1986)
47. M Eckel, D Ottenwalder, F Scholz, G Frankowsky, T Wacker, Y Hangleiter *Appl. Phys. Lett.* **64** 854 (1994)
48. S J W Price, J P Richard, R C Rumfeld *Can. J. Chem.* **51** 1397 (1973)
49. M C Paputa, S J W Price *Can. J. Chem.* **57** 3178 (1979)
50. W L Gladfelter, D C Boyd, K F Jensen *Chem. Mater.* **1** 339 (1989)
51. D B Beach, S E Blum, F K LeGoues *J. Vac. Sci. Technol. A, Vac. Surf. Films* **7** 3117 (1989)
52. L H Dubois, B R Zegarski, C T Kao, R G Nuzzo *Surf. Sci.* **236** 77 (1990)
53. A Kohzen, Y Tohmori, Y Akatsu, H Kamada *J. Cryst. Growth* **124** 70 (1992)
54. J Han, K F Jensen, Y Senzaki, W L Gladfelter *Appl. Phys. Lett.* **64** 425 (1994)
55. G W Fraser, N N Greenwood, B P Straughan *J. Chem. Soc.* 3742 (1963)
56. G N Nechiporenko, L B Petukhova, A S Rozenberg *Izv. Akad. Nauk SSSR, Ser. Khim.* 1697 (1975)
57. L H Dubois, B R Zegarski, M E Cross, R G Nuzzo *Surf. Sci.* **244** 89 (1991)
58. H Protzmann, T Marschner, O Zsebok, W Stolz, E O Gobel, R Dorn, J Lorberth *J. Cryst. Growth* **115** 248 (1991)
59. V Souliere, P Abraham, I Bouix, M P Berthet, Y Monteil, A M Pougnet, R Mellet, A Ougazzaden, A Mircea *J. Cryst. Growth* **124** 93 (1992)
60. P B Ayscough, H J Emeleus *J. Chem. Soc.* 3381 (1954)
61. S J W Price, J P Richard *Can. J. Chem.* **48** 3209 (1970)
62. V A Yablokov, I A Zelyaev, E I Makarov, Yu F Gatilov, V A Gonina, A D Zorin *Zh. Obshch. Khim.* **56** 365 (1986)
63. V A Yablokov, I A Zelyaev, E I Makarov, V A Gonina, E N Karataev *Poluchenie i Analiz Chistykh Veshchestv* (The Preparation and Analysis of Pure Substances) (Gor'kii: Izd. Gorkovsk. Gos. Univ., 1988) p. 33
64. A E Sokolovskii, A K Baev, V I Bludilina, Yu L Gubar' *Metalloorg. Khim.* **1** 1323 (1988)
65. S J W Price, J P Richard *Can. J. Chem.* **50** 966 (1972)
66. S J W Price, A F Trotman-Dickenson *Trans. Faraday Soc.* **54** 1630 (1958)
67. V A Yablokov, I A Zelyaev, E I Makarov, N S Lokhov *Zh. Obshch. Khim.* **57** 2034 (1987)
68. V A Yablokov, I A Zelyaev, N S Lokhov, E I Makarov *Zh. Obshch. Khim.* **54** 1549 (1984)
69. V A Yablokov, I A Zelyaev, E I Makarov, A V Dozorov, in *Abstracts of the XIIIth International Conference on Organometallic Chemistry, Torino, Italy, 1988* p. 351
70. V A Yablokov, I A Zelyaev, E I Makarov, in *Tez. Dokl. IV Vsesoyuz. Konf. po Metalloorganicheskoi Khimii* (Abstracts of Reports at the IVth All-Union Conference on Organometallic Chemistry) (Kazan': Izd. Kazan'sk. Gos. Univ., 1988) Vol. 2, p. 64
71. G P Smith, R Patrick *Int. J. Chem. Kinet.* **15** 167 (1983)
72. S G Yudenich, O N Druzhkov, N M Uvarova, V A Dodonov *Zh. Obshch. Khim.* **53** 2548 (1983)
73. S H Li, C A Larsen, G B Stringfellow *J. Cryst. Growth* **112** 515 (1991)
74. S R Kurtz, J M Olson, A Kibbler *J. Electron. Mater.* **18** 15 (1989)
75. E A Beam, T S Henderson, A C Seabaugh, I Y Yang *J. Cryst. Growth* **116** 436 (1992)
76. G Hincelin, M Zahzouh, R Mellet, A M Pougent *J. Cryst. Growth* **120** 119 (1992)
77. C H Chen, C A Larsen, G B Stringfellow, D W Brown, A J Robertson *J. Cryst. Growth* **77** 11 (1986)
78. C A Larsen, N I Buchan, S H Li, G B Stringfellow *J. Cryst. Growth* **94** 663 (1989)
79. S H Li, N I Buchan, C A Larsen, G B Stringfellow *J. Cryst. Growth* **98** 309 (1989)
80. C A Larsen, N I Buchan, S H Li, G B Stringfellow *J. Cryst. Growth* **94** 673 (1989)
81. S H Li, N I Buchan, C A Larsen, G B Stringfellow *J. Cryst. Growth* **96** 906 (1989)
82. S H Li, C A Larsen, N I Buchan, G B Stringfellow *J. Electron. Mater.* **18** 457 (1989)
83. G H Fan, R D Hoare, M E Pemble, I M Povey, A G Taylor, J O Williams *J. Cryst. Growth* **124** 49 (1992)
84. M Harrous, L Chaput, A Bendraoui, M Cadoret, C Pariset, R Cadoret *J. Cryst. Growth* **92** 423 (1988)

85. V A Yablokov, S V Mitrofanova, S Ya Knyazhanskii *Zh. Obshch. Khim.* **64** 1113 (1994)
86. G Zimmermann, H Plotzmann, W Stolz, E O Gobel, P Gimmnich, A Greiling, J Lorberth, C Thalmann, K Rademann *J. Cryst. Growth* **136** 142 (1992)
87. C H Chen, K T Huang, D L Drobeck, G B Stringfellow *J. Cryst. Growth* **124** 142 (1992)
88. C H Chen, G B Stringfellow, D C Gordon, D W Brown, B A Vaartstra *Appl. Phys. Lett.* **62** 204 (1992)
89. O Yu Okhlobystin *Usp. Khim.* **36** 34 (1967) [*Russ. Chem. Rev.* **36** 17 (1967)]
90. S Brownstein, B S Smith, G Erlich, A W Laubengayer *J. Am. Chem. Soc.* **81** 3826 (1959)
91. G E Coates *J. Chem. Soc.* 2003 (1951)
92. G E Coates, in *Organometallic Compounds* Vol. 1 (Eds G E Coates, M L H Green, K Wade) (London: Methuen, 1967) p. 307
93. W LeVason, C A McAuliffe *Coord. Chem. Rev.* **19** 173 (1976)
94. V A Yablokov, A V Dozorov, V M Kharchevnikov *Metalloorg. Khim.* **1** 638 (1988)
95. V A Yablokov, A V Dozorov, S V Mitrofanova, B S Yavich *Zh. Obshch. Khim.* **59** 2268 (1989)
96. V A Yablokov, A V Dozorov, S V Mitrofanova, B S Yavich *Zh. Obshch. Khim.* **60** 574 (1990)
97. V A Yablokov, A V Dozorov, S V Mitrofanova, B S Yavich *Metalloorg. Khim.* **4** 762 (1991)
98. A T Carli, P Gibart, R Druilhe, Y Monteil, J Bouix, B Eljani *Rev. Phys. Appl.* **20** 569 (1985)
99. E A Piocos, B S Ault *J. Am. Chem. Soc.* **111** 8978 (1989)
100. D J Schlyer, M A Ring *J. Organomet. Chem.* **114** 9 (1976)
101. J Nishizawa, T Karabaashi *J. Electrochem. Soc.* **130** 413 (1983)
102. M Mashita, S Horiguchi, M Shimazu, K Kamon, M Mihara, M Ishii *J. Cryst. Growth* **77** 194 (1986)
103. M R Leys, H Veenvliet *J. Cryst. Growth* **55** 145 (1981)
104. R Didchenko, J E Alix, R H Toeniskoetter *J. Inorg. Nucl. Chem.* **14** 35 (1960)
105. J P Noad, A J Springthorpe *J. Electron. Mater.* **9** 601 (1980)
106. C H Cheng, K A Jones, K M Morn *J. Electron. Mater.* **13** 703 (1984)
107. I A Frolov, E M Kitaev, B L Druz', E V Sokolov *Zh. Fiz. Khim.* **51** 1106 (1977)
108. K Tamaru *J. Phys. Chem.* **59** 777 (1955)
109. K C Williams, T L Brown *J. Am. Chem. Soc.* **88** 5460 (1966)
110. E G Hoffman *Trans. Faraday Soc.* **58** 642 (1962)
111. T F Kuech, E Veuhoff *J. Cryst. Growth* **68** 148 (1984)
112. R Bhat *J. Electron. Mater.* **14** 433 (1985)
113. T F Kuech, E Veuhoff, T S Kuan, V Deline, R Potemski *J. Cryst. Growth* **77** 257 (1986)
114. D J Schyer, M A Ring *Solid State Sci. Technol.* **124** 569 (1977)
115. J E Butler, N Bottka, R S Sillmon, D K Gaskill *J. Cryst. Growth* **7** 163 (1986)
116. C P Kuo, R M Cohen, G B Stringfellow *J. Cryst. Growth* **64** 461 (1983)
117. D H Reep, S K Chandhi *J. Electrochem. Soc.* **130** 675 (1983)
118. P B Boldyrevskii, V G Parashkov, A A Krasnov, S L Tkachenko, V A Usnov *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** 1077 (1986)
119. G Arens, M Heyen, H Luth, P Balk *Thin Solid Films,* **136** 281 (1986)
120. G Arens, H Heinecke, N Putz, P Luth, P Balk *J. Cryst. Growth* **76** 305 (1986)
121. S R Armstrong, R D Hoare, M E Pemble, I M Povey, A Stafford, A G Taylor, J O Williams *J. Cryst. Growth* **124** 10 (1992)
122. M Hoshino *J. Cryst. Growth* **110** 704 (1991)
123. N Kahayashi, Y Yamauchi, Y Horikoshi *J. Cryst. Growth* **115** 353 (1991)
124. N Kahayashi, Y Horikoshi *Jpn. J. Appl. Phys.* **28** L1880 (1989)
125. G A Domrachev, L I Zakharov, Yu A Shevelev *Usp. Khim.* **54** 1260 (1985) [*Russ. Chem. Rev.* **54** 739 (1985)]
126. G A Domrachev, V D Zinov'ev *Usp. Khim.* **47** 679 (1978) [*Russ. Chem. Rev.* **47** 354 (1978)]
127. G A Razuvaev (Ed.) *Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov* (The Use of Organometallic Compounds for the Preparation of Inorganic Coatings and Materials) (Moscow: Nauka, 1986)
128. *Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov (Tez. VI Vsesoyuz. Soveshch.) Nizhnii Novgorod, 1991* [The Use of Organometallic Compounds for the Preparation of Inorganic Coatings and Materials (Abstracts of the VIth All-Union Meeting) Nizhnii Novgorod, 1991]