

Features of Joint Thermolysis of Organometallic Compounds of Group III and V Elements

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Abstract—The kinetic data on thermolysis of equimolar gaseous mixtures of organometallic compounds of Group III and V elements show that the thermal stability of the mixture differs from that of the components taken separately, which is mainly due to complexation between the mixture components. The complex is a kinetically active species. The rate of joint thermolysis of the organometallic compounds grows as the number of hydride atoms at the Group V element increases in the order $\text{AsMe}_3 < t\text{-BuPH}_2 < \text{AsH}_3$. The stability of the complexes formed by organometallic compounds of Group III and V elements decreases in the same order. Joint thermolysis of Me_3Ga and AsH_3 yields a solid oligomer $\text{Me}_2\text{GaAs(H)Ga(Me)AsH}_2$. The complicated pattern of decomposition of a mixture of trimethylaluminum with various electron donors is due to participation in the pyrolysis of two trimethylaluminum species: monomeric and dimeric. In decomposition of pure trimethylaluminum or its mixtures with organometallic compounds of Group V elements or with ether, solid pyrolysis products deposited on the vessel walls catalyzed further transformations of the mixture components.

High-purity alkyl derivatives and hydrides of Group III and V elements are important precursors in preparation of semiconducting epitaxial structures for micro- and optoelectronics. The advantages of pyrolytic deposition of coatings using organometallic compounds are simple and efficient process, possibility of its full automation, high quality of the coatings, and the possibility of preparing coatings of various compositions and preset properties on substrates of diverse shapes [1–3].

The goal of this study was to analyze the general features of thermal decomposition of pure organometallic compounds of Group III and V elements and of equimolar mixtures of these under comparable conditions on the basis of published data and to study the process in detail for a mixture of Me_3Ga with AsH_3 as specific example. The kinetic experiment was performed as described in [4, 5].

Thermolysis of Me_3Al follows the first-order kinetics up to ~30% conversion [5]. The Arrhenius dependence of the rate constant is as follows:

$$\ln k = (39.3 \pm 13.2) - (198 \pm 34) \times 10^3 / (8.31T).$$

When the reactor walls are coated with a film of solid decomposition products of Me_3Al , the kinetic pattern changes. The thermolysis follows the first-order kinetics up to 65% conversion; at 611 K, $k = (22.6 \pm 0.3) \times 10^{-5} \text{ s}^{-1}$. Both monomeric and dimeric

forms of Me_3Al participate in the pyrolysis. Pyrolysis of Me_3Al is accompanied by evolution of methane and deposition of an organoaluminum polymer on the reactor surface. This product catalyzes further transformations of Me_3Al . Scheme 1 shows possible reactions occurring in the course of Me_3Al pyrolysis in the reactor volume and on its walls. The contribution of each thermolysis pathway is determined by the temperature-dependent factors: shift of the dimer–monomer equilibrium (equilibrium constant K) and variation of the rate constant of elimination of methyl groups from the dimer (k_1) and monomer (k'_1).

The thermal decomposition of Me_3Ga (675–718 K), Me_3In (556–598 K), Et_3In (456–483 K), and also of H_3As (684–722 K) and Me_3As (702–736 K), follows the first-order kinetics [6–10]. The Arrhenius dependences of the pyrolysis rate constants are as follows:

$$\ln k_{\text{Me}_3\text{Ga}} = (23.1 \pm 2.1) - (178.7 \pm 4.3) \times 10^3 / (8.31T), \quad (1)$$

$$\ln k_{\text{Me}_3\text{In}} = (22.5 \pm 2.0) - (149 \pm 4.8) \times 10^3 / (8.31T), \quad (2)$$

$$\ln k_{\text{Et}_3\text{In}} = (27.1 \pm 1.9) - (137 \pm 3.5) \times 10^3 / (8.31T), \quad (3)$$

$$\ln k_{\text{AsH}_3} = (14.4 \pm 3.6) - (128.1 \pm 21) \times 10^3 / (8.31T), \quad (4)$$

$$\ln k_{\text{AsMe}_3} = (36.2 \pm 4.3) - (258.7 \pm 12.6) \times 10^3 / (8.31T). \quad (5)$$

The activation energy is expressed in J mol^{-1} . Our results are nicely consistent with published data (see references in [3]).

Scheme 1.

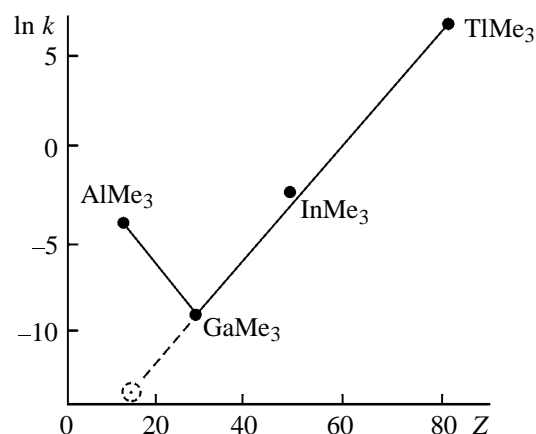
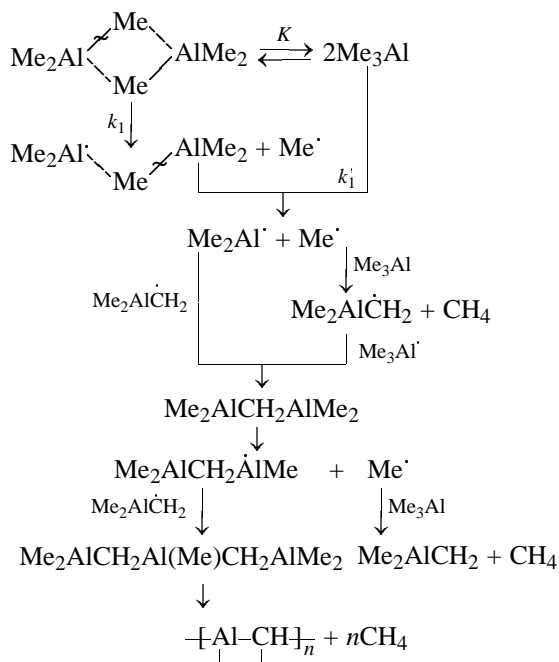


Fig. 1. Correlation of the rate constants of pyrolysis of Group III metal methyl derivatives at 688 K with the metal atomic number Z . The point denoted by dashed line corresponds to the possible $\ln k$ value for monomeric Me_3Al .

Correlation of the pyrolysis rate constants with the metal atomic number Z for methyl derivatives of Group III metals at 688 K shows that, for pure Me_3Al , k should be considerably (by almost four orders of magnitude) lower than our experimental value of $1.3 \times 10^{-2} \text{ s}^{-1}$. Namely, it should be equal to $4 \times 10^{-6} \text{ s}^{-1}$. We believe that the outlying location of the point for Me_3Al in the $\ln k$ - Z coordinates (Fig. 1) is due to participation of both monomeric and dimeric Me_3Al species in pyrolysis. The three-centered bonding in the dimer weakens the Al-Me bond, and the thermolysis rate grows. The degree of dimerization of Me_3Al depends on temperature; therefore, the temperature range of decomposition of this compound is very wide, and the kinetic and activation parameters of the decomposition reported in different papers [3] differ very significantly.

It was suggested recently to use less toxic Group V element derivatives, e.g., *tert*-butylphosphine, for deposition of semiconducting films. We found [4] that thermal decomposition of *t*-BuPH₂ is described by a first-order kinetic equation to 60–70% conversion. This is a pseudo-first-order reaction. The rate constant *k* depends on the initial pressure *P*₀, gradually increasing from 78.7 × 10^{−5} s^{−1} at 40 mm Hg to 201.3 × 10^{−5} s^{−1} at 342 mm Hg (626 K). The temperature dependence of the thermolysis rate of *t*-BuPH₂ was studied in the range 593–626 K at *P*₀ 170–199 mm Hg. The activation energy of the reaction is 158.8 ± 5.4 kJ mol^{−1}, ln *k*₀ 23.9 ± 2.1.

The rate and mechanism of pyrolysis of a mixture

of organometallic compounds depend on the contribution of their donor-acceptor interaction to the process. Mixing of Me_3Ga with Me_3As increases the rate of their thermolysis by a factor of 1.5–2 compared to pure organometallic compounds. Therefore, to understand the kinetics of joint decomposition of organometallic compounds of Group III and V elements, it is useful to know the thermodynamic characteristics of their donor-acceptor complexes.

The stable complexes $\text{Me}_3\text{Al} \cdot \text{AsMe}_3$, $\text{Me}_3\text{Ga} \cdot \text{AsMe}_3$, $\text{Me}_3\text{In} \cdot \text{AsMe}_3$, and $\text{Me}_3\text{Al} \cdot \text{PH}_2\text{Bu-}t$ were prepared; their dissociation constants K_d and enthalpies of dissociation ΔH were calculated (see table), and possible concentrations of complexes at the temperatures of thermolysis of organometallic compounds were estimated [5, 9, 10].

At room temperature, the complexes are fairly stable. Above 350 K, they dissociate to the initial organometallic compounds. Their dissociation in the gas phase in the range 350–480 K was studied. The tendency of the complexes to dissociate into the components grows in the order $\text{Me}_3\text{Al} \cdot \text{AsMe}_3 < \text{Me}_3\text{Al} \cdot \text{H}_2\text{P}^i\text{Bu}-t < \text{Me}_3\text{In} \cdot \text{AsMe}_3 < \text{Me}_3\text{Ga} \cdot \text{AsMe}_3$. For example, the $K_d \times 10^2$ values of these compounds at 430 K are 21.5, 36.1, 101.5, and 351.2 atm, respectively. The stability of the complexes grows with increasing number of alkyl groups and decreases with increasing number of hydride atoms at the Group V element. Above 480 K, the mixture of gaseous organometallic compounds decomposes irreversibly in the gas phase and on the reactor surface.

Thermodynamic characteristics of complexes formed by organometallic compounds of Group III and V elements

Compound	<i>T</i> , K	<i>P</i> , atm	<i>P</i> ₀ , atm	α	<i>K</i> _d × 10 ² , atm	Δ <i>H</i> , kJ mol ⁻¹
Me ₃ Al · AsMe ₃	450.2	0.37	0.22	0.77	54.0	65.5 ± 0.5
Me ₃ Ga · AsMe ₃	450.2	0.25	0.128	0.98	674	43.2 ± 1.2
Me ₃ In · AsMe ₃	451.1	0.35	0.185	0.92	204	50.1 ± 0.5
Me ₃ Al · BuPH ₂	384	0.088	0.058	0.58	4.52	63.7 ± 1.5

^a (*P*, *P*₀) Pressure of the gaseous complex, measured experimentally and calculated theoretically from the equation of state of the ideal gas, respectively; (α) degree of dissociation of gaseous complexes of organometallic compounds; ampule volume 114 cm³.

Data are available on the kinetic features of thermolysis (500–750 K) of mixtures of Me₃Al with Me₃As [11], diethyl ether [5], and *t*-BuPH₂ [10]; of Me₃Ga with Me₃As [6], H₃As, and *t*-BuPH₂ [4]; and of Me₃In with Me₃As [12].

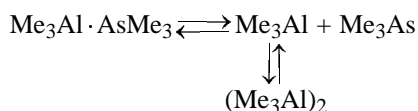
The presence of such electron donors as Me₃As, diethyl ether, or *t*-BuPH₂ strongly affects the pattern of Me₃Al thermolysis. It is noted that the thermal stability of Me₃Al increases in the presence of donors [5, 10, 11].

The thermolysis of Me₃Al mixed with Me₃As follows a first-order kinetics up to 70–80% conversion (*k*₁, s⁻¹). The Arrhenius dependences of the rate constants of thermolysis of Me₃Al and Me₃As in their mixture are, respectively, as follows:

$$\ln k_1 \text{ (s}^{-1}\text{)} = (14.8 \pm 4.4) - (122.6 \pm 13) \times 10^3 / (8.31T), \quad (6)$$

$$\ln k_2 \text{ (s}^{-1}\text{)} = (35.9 \pm 3.6) - (250.8 \pm 6.1) \times 10^3 / (8.31T). \quad (7)$$

The fact that the rate constant of thermolysis of Me₃As in the absence of Me₃Al [Eq. (5)] coincides with that in the presence of Me₃Al [Eq. (7)] shows that thermolysis of Me₃As is independent of the presence of Me₃Al. On the contrary, the presence of Me₃As strongly affects the decomposition of Me₃Al. Firstly, decomposition of Me₃Al in the mixture follows the first-order kinetics to higher conversions; secondly, the thermal stability of Me₃Al is enhanced (the temperature range of Me₃Al decomposition shifts from 610–620 to 680–730 K). Below 420–470 K, the unsaturated vapor in the reaction vessel is an equilibrium mixture:



With increasing temperature, the complex Me₃Al · AsMe₃ and the dimer (Me₃Al)₂ dissociate to individual monomeric species. At the temperatures of decomposition of the organometallic compounds (670–730 K), the equilibrium concentrations of the dimer

(Me₃Al)₂ and complex Me₃Al · AsMe₃ become insignificant. However, from the kinetic viewpoint, if the complex is a kinetically active species, even insignificant amounts of the complex Me₃Al · AsMe₃ may be sufficient to provide a major contribution of this pathway to the overall process. Trimethylarsine shifts the equilibrium (Me₃Al)₂(g) \rightleftharpoons Me₃Al(g). The concentration of trimethylaluminum dimers decreases owing to formation of the complex Me₃Al · AsMe₃. In this case, monomeric Me₃Al and Me₃Al bound in a complex with Me₃As play the major role in thermolysis. Trimethylaluminum behaves as a “monomer” both in the free state and in the complex with Me₃As. This fact accounts for the lower rate of Me₃Al decomposition in the presence of AsMe₃ by the first-order reaction.

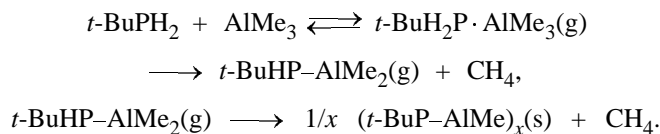
Addition to Me₃Al of other electron donors also decreases the concentration of trimethylaluminum dimer and results in decomposition of Me₃Al by the first-order reaction [5]. For example, the rate constants of thermolysis of Me₃Al in a mixture with ether in the initial reaction period are close to the constants of Me₃Al decomposition in the presence of Me₃As [Eqs. (6), (8)].

$$\ln k_1 \text{ (s}^{-1}\text{)} = (15.4 \pm 4.9) - (123.6 \pm 19.3) \times 10^3 / (8.31T). \quad (8)$$

The results confirm our assumption that the complexation of Me₃Al with both Me₃As and ether decreases the content of dimeric trimethylaluminum and decelerates the pyrolysis of Me₃Al. Similar to decomposition of pure Me₃Al, decomposition of its mixtures with organometallic compounds of Group V elements or with ether is catalyzed by the thermolysis products deposited on the vessel walls [5].

Irreversible decomposition of the equilibrium gaseous mixture of Me₃Al with *t*-BuPH₂ starts at temperatures that are considerably lower than the decomposition points of the pure compounds [10]. The gas evolution curves are S-shaped, owing to the processes occurring both in the gas phase and on the reactor walls. The complex *t*-BuPH₂ · AlMe₃ is stable at room temperature, but above 300 K it dissociates in the gas

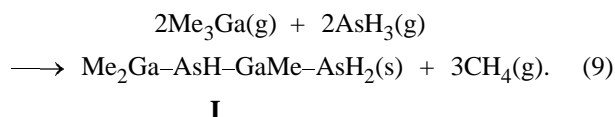
phase to the initial organometallic compounds. At 498–511 K, the components are consumed in the following reactions:



This is confirmed by GLC analysis of the products. About 2 mol of CH_4 is released per mole of the starting compounds, and polymeric products are deposited on the reactor walls. For deeper thermolysis of the reaction mixture, the temperature should be increased to 594–604 K. The polymeric products deposited on the reactor walls decompose in this range. Among gaseous products, methane, hydrogen, butane, and butene were detected [10].

The kinetics of the reaction of Me_3Ga with AsH_3 was studied in detail by Larsen *et al.* [13]. They concluded that the reaction occurs both in the gas phase and on the surface and that it strictly follows the 1 : 1 stoichiometric ratio. The possible reaction mechanism involves formation of an adduct by the initial components. As believed by Larsen *et al.* [13], the limiting stage is decomposition of Me_3Ga .

We found that mixing of individual Me_3Ga and AsH_3 in a 1 : 1 ratio results in formation of the oligomer. At 289.4 K, the pressure in the vessel of constant volume (V 25 cm^3) slowly decreases, flattening out at the level of 75% of the initial pressure. After reaction completion, only methane was detected in the gas phase; its amount corresponded to the stoichiometry of Eq. (9) (Fig. 2, curve 1). In the experiments performed at similar temperatures (288.8 and 289.2 K) but different initial pressures of the organometallic compound (160 and 204 mm), the pressure in the reaction vessel also decreased by 25%.



Formation of oligomer **I** is complete within ~1 h after mixing gaseous organometallic compounds. According to GLC and IR data, the only gaseous product after the reaction completion is methane (3 mol). We detected in the gas phase neither unchanged Me_3Ga and AsH_3 , nor other volatile products containing Ga or As atoms. The amount of the evolved methane exactly corresponds to the stoichiometric equation of reaction (9). Thus, the oligomer $\text{Me}_2\text{Ga}[\text{AsH-GaMe}]_x\text{AsH}_2$ is deposited on the reactor walls; it is a light gray solid stable at 289 K.

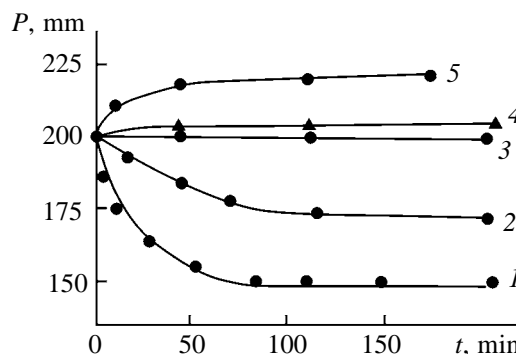


Fig. 2. Variation with time t of the pressure P of equimolar gaseous mixtures of Me_3Ga and AsH_3 . T , K: (1) 289, (2) 298, (3) 332, (4) 338, and (5) 353.

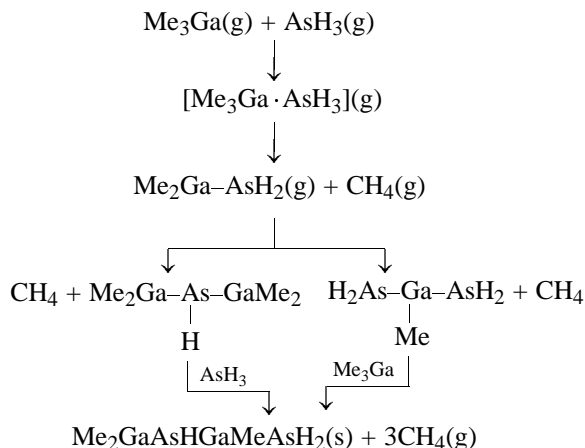
The thermal decomposition of **I** on the reactor walls was studied in the range 414–424 K. The reaction follows the first-order kinetics. The temperature dependence of the rate constant is as follows:

$$\ln k = (23.2 \pm 4) - (103.5 \pm 1.7) \times 10^3 / (8.317T).$$

Thermolysis of **I** yields 1 mol of methane. The color of the polymeric film changes from light gray to brown, and a mixture of oligomers with a higher molecular weight is formed on the surface.

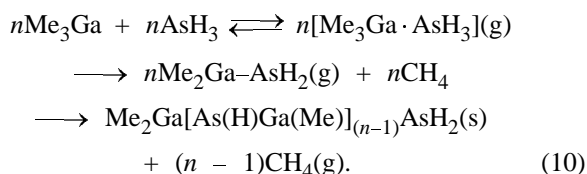
Plocos and Ault [14, 15] studied the IR spectra of a mixture of Me_3Ga and AsH_3 in Ar and N_2 matrices and proved formation of the complex $\text{Me}_3\text{Ga} \cdot \text{AsH}_3$. Sennikov *et al.* [16] found that the donor-acceptor complex exists in solution in liquid Kr, whereas at 263 K the components react at a noticeable rate to form $\text{Me}_{3-x}\text{GaAsH}_{3-x}$. Therefore, our results in combination with published data suggest the following pathway of formation of **I** at temperatures close to room temperature.

Scheme 2.

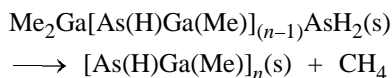


The primary event in the reaction of Me_3Ga with AsH_3 is formation of the gaseous complex $\text{Me}_3\text{Ga} \cdot \text{AsH}_3$, which is unstable at 289 K and decomposes to give one CH_4 molecule and gaseous $\text{Me}_2\text{Ga}-\text{AsH}_2$. The latter transforms into solid oligomer **I** by reacting with molecules of the initial compounds, as shown in Scheme 2.

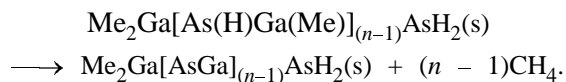
The condensation and subsequent oligomerization of Me_3Ga and AsH_3 can be described by the following general equation:



At $n=2$, the process is completed with formation of oligomer **I**. If the reactants are mixed at higher temperatures, the oligomerization goes further, and products with a higher molecular weight are formed. The degree of condensation can be judged from the amount of the evolved CH_4 . As the oligomeric chain propagates, i.e., as the number of units $(n-1)$ increases, the difference between the amounts of the reacted Me_3Ga and AsH_3 (in moles) and that of the evolved CH_4 (in moles) decreases. As seen from Fig. 2, when the reactants are mixed at 298 K, the pressure drop in the reaction system after mixing is 16% (Fig. 2, curve 2), which, according to (10), corresponds to $n=6$. At large n , $(n-1) \approx n$. At 332 and 338 K (curves 3 and 4, respectively), the reaction is not accompanied by significant changes in the pressure, and the only apparent evidence of its occurrence is formation of a polymeric film. When the reaction of Me_3Ga with AsH_3 is performed at 353 K (curve 5), the pressure build-up becomes noticeable; this is due to the following reactions (at $n \rightarrow \infty$):



or



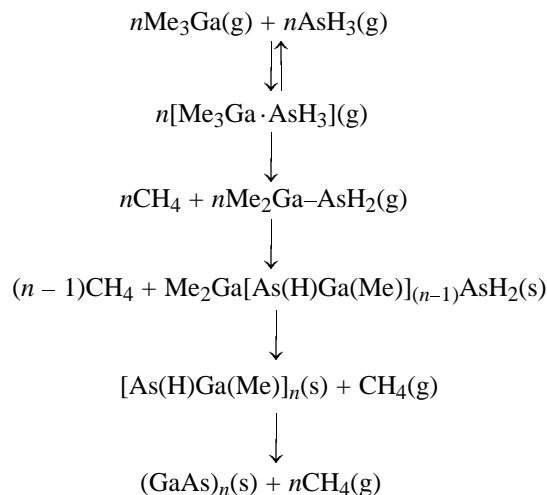
In the range 604–633 K, the oligomers on the surface of the reaction vessel decompose, an additional 0.5 mol of methane is evolved, and the film turns black. The growth of the molecular weight of the oligomer follows the first-order kinetics; the Arrhenius dependence of k on temperature is as follows:

$$\ln k = (25.6 \pm 6.3) - (171 \pm 28) \times 10^3 / (8.31T).$$

The total amount of methane released from 1 mol of Me_3Ga is 3 mol.

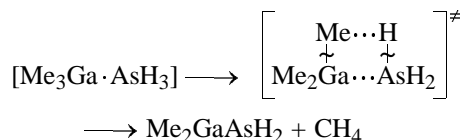
The thermal decomposition of a mixture of Me_3Ga with AsH_3 presumably involves the following successive and parallel reactions:

Scheme 3.



Under conditions of metal-organic chemical vapor deposition (MOCVD), a reaction mixture flows to a heated support and passes several temperature zones. Apparently, the species that reach the heated surface are oligomers and their pyrolysis products, rather than individual organometallic compounds.

The initial stage is formation of the unstable complex $\text{Me}_3\text{Ga} \cdot \text{AsH}_3$. The complex is a kinetically active species:



Pyrolysis of an equimolar mixture of Me_3In and Me_3As becomes noticeable at 570 K [12, 17], which corresponds to the onset temperature of decomposition of pure Me_3In . The pyrolysis was performed in two steps: in the ranges 576–601 and 668–682 K. In the first range, Me_3In decomposes. The temperature dependence of k is as follows:

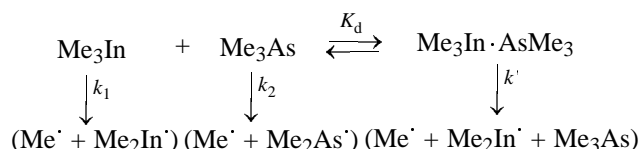
$$\ln k = (13.7 \pm 3.5) - (103.2 \pm 8.5) \times 10^3 / (8.31T).$$

The k values in this range are approximately two times higher than in pyrolysis of pure Me_3In . As judged from the pressure build-up in the system, in this temperature range Me_3As does not decompose.

At a higher temperature (668–682 K), the mixture undergoes further thermolysis. The kinetic curves are described by a first-order equation, with the k values being approximately two times higher than in thermolysis of pure Me_3As . The temperature dependence of the rate constants of thermolysis of Me_3As in a mixture with Me_3In is as follows:

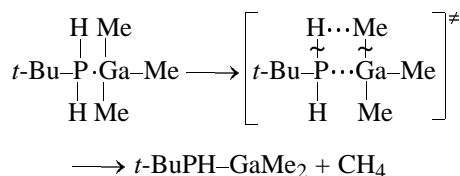
$$\ln k = (29.1 \pm 4.0) - (214.2 \pm 11.2) \times 10^3 / (8.31T).$$

Hence, the presence of Me_3In in the mixture affects the decomposition of Me_3As . In a stoichiometric mixture of Me_3In with Me_3As , the components promote the pyrolysis of each other. The measured overall rate constant k includes the decomposition constants of pure Me_3In and the complex $\text{Me}_3\text{In} \cdot \text{AsMe}_3$:



The stoichiometric gaseous mixture of Me_3Ga with Me_3As decomposes similarly [9]. However, in contrast to the mixtures of Me_3Al and Me_3In with Me_3As , the decomposition products do not catalyze pyrolysis of Me_3Ga and its mixtures with organometallic compounds of Group V elements [17].

Thus, organometallic derivatives of Group III and V elements affect the thermolysis of each other, and differences in their thermal stability are leveled off. We believe that this is mainly due to complexation between the components. The complex is a kinetically active species. The structure of the complexes $\text{R}_3\text{M(III)} \cdot \text{M(V)}\text{R}_3'$ or $\text{R}_3\text{M(III)} \cdot \text{M(V)}\text{H}_3$ provides formation in the limiting stage of an activated state in which the cleavage of the $\text{R}-\text{M(III)}$, $\text{R}-\text{M(V)}$, and $\text{M(V)}-\text{H}$ bonds is facilitated energetically and sterically. For example, in joint decomposition of $t\text{-BuPH}_2$ and Me_3Ga , complexation causes weakening of the $\text{Me}-\text{Ga}$ and $\text{P}-\text{H}$ bonds.



The sterically favorable location of the methyl group in the vicinity of the hydrogen atom of *tert*-butylphosphine in the complex facilitates elimination of the methane molecule.

The mutual effect of the mixture components in joint decomposition becomes stronger with increasing

number of hydride atoms at the Group V element: $\text{AsMe}_3 < t\text{-BuPH}_2 < \text{AsH}_3$. The stability of the complexes formed by the organometallic compounds of Group III and V elements decreases in the same series.

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