

MASS SPECTROMETRIC STUDY OF $\text{Hf}(\text{O}^t\text{Bu})_2(\text{mmp})_2$ THERMAL DECOMPOSITION

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Abstract. Thermal stability of a new promising precursor for HfO_2 MOCVD, $\text{Hf}(\text{O}^t\text{Bu})_2(\text{mmp})_2$, was studied by mass spectrometry in a temperature range from 25 to 450 °C at pressure varying from 0.5 to 5 Torr. The onset of gaseous $\text{Hf}(\text{O}^t\text{Bu})_2(\text{mmp})_2$ thermal decomposition was found to occur at a temperature of about 300 °C. The Arrhenius function $k(T) = k_0 \exp(-E_a/RT)$ was used to describe the temperature effect on the precursor decomposition at 300-350 °C; the values of the activation energy $E_a = 92.14$ kJ/mol and $k_0 = 1.25 \cdot 10^6$ 1/s are recommended for this temperature range. Possible decomposition mechanisms are discussed.

1. INTRODUCTION

Metal organic compounds with a four-coordinate central hafnium atom, such as $\text{Hf}(\text{NEt}_2)_4$ [$\text{Hf}(\text{N}(\text{C}_2\text{H}_5)_2)_4$] and $\text{Hf}(\text{O}^t\text{Bu})_4$ [$\text{Hf}(\text{OC}_4\text{H}_9)_4$], are considered to be perspective precursors for HfO_2 metal organic chemical vapor deposition (MOCVD) due to their thermal stability and high vapor pressure [1-3]. On the other hand, Hf is known to possess a higher coordinate number of six, seven or even eight (see e.g. [4]), so one can suggest that the metal centers in these precursors are unsaturated. This, in turn, gives rise to an extremely high air and moisture sensitivity of the precursors, making them difficult to store and handle and setting a number of limitations on their use in MOCVD.

A novel hafnium precursor $\text{Hf}(\text{O}^t\text{Bu})_2(\text{mmp})_2$, having a six-coordinate central Hf atom due to two bidentate alcoxide ligands, has been found to be much more stable to air and moisture [4]. More-

over, being monomeric, it possesses high vapor pressure in contrast to most of metal alcoxide precursors which were found to be polymeric. However, the information on the $\text{Hf}(\text{O}^t\text{Bu})_2(\text{mmp})_2$ physico-chemical properties is quite poor in available literature. Williams *et al.* in [4] presented some preliminary results on the crystal structure of the solid precursor molecule and compared the oxide film growth rates from Hf- and Zr-containing precursors. Good dielectric properties of the films were mentioned. Unfortunately, this work is a brief report only and its data are rather fragmentary. Obviously, the properties of $\text{Hf}(\text{O}^t\text{Bu})_4$ [5,6] can be used as a basis for $\text{Hf}(\text{O}^t\text{Bu})_2(\text{mmp})_2$ investigation, but the differences induced by four- and six-coordinate central Hf atoms should be accounted for to compare these compounds consistently.

Thus, one can conclude that the information on $\text{Hf}(\text{O}^t\text{Bu})_2(\text{mmp})_2$ is quite insufficient for MOCVD technology. Since the data on the precursor ther-

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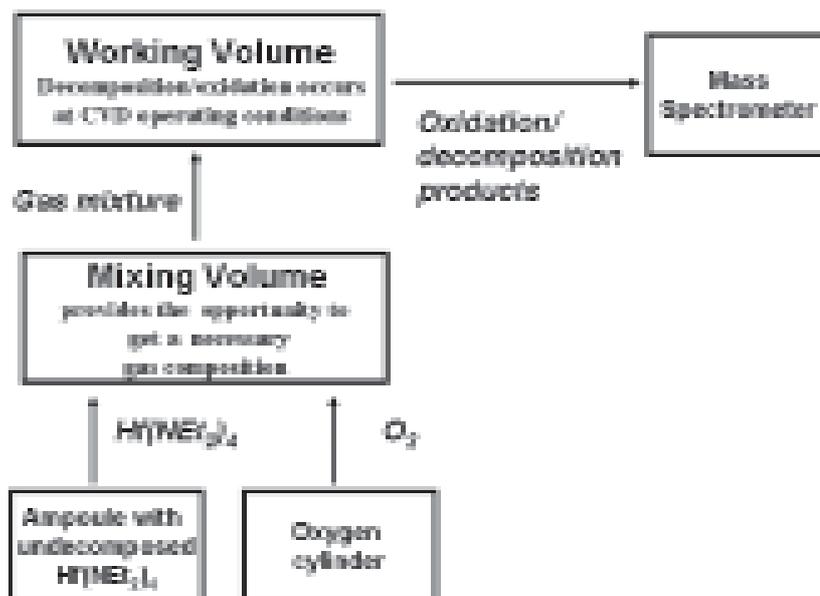


Fig. 1. A scheme of the experimental setup.

mal decomposition are of first-priority here, this paper focuses on the study of the thermal decomposition of gaseous $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ under the operating conditions typical for MOCVD reactors.

2. EXPERIMENTAL

A scheme of the installation used in our study is presented in Fig. 1. The experimental procedure can be briefly described as follows. An undecomposed precursor supplied by INORGTECH was loaded into a stainless steel ampoule in argon (99.95%) to prevent possible interaction with oxygen or water vapor. The manifold system connecting the ampoule with the working volume includes a needle valve unit, which provides the required $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ pressure in the working volume, and a set of intermediate volumes. Preliminary runs were carried out to optimize the experimental conditions. The key problems at this stage were the suppression of a possible precursor condensation on the cold walls of the supply system and the choice of a temperature regime that gives an opportunity to avoid the precursor decomposition in the ampoule and supply system. In addition, the temperature uniformity in the working volume was tested. Table 1 describes the typical temperature regime used in the present study.

Undecomposed precursor was then flooded into the pre-evacuated working volume maintained at a given temperature. Since the total volume of the intermediate units was ~ 15 times larger than the working volume, we believe that the initial pressure in the working volume after the precursor flooding differed by $\pm 10\%$ from the value measured by a PMT-2 gauge head placed at the mixing volume wall. The temperature of the working volume was measured by a Pt-PtRh thermocouple welded directly to the outer wall of the unit. The gas composition in the working volume was examined by a commercial MI 1201T magnetic sector-field mass spectrometer with the main characteristics listed below.

- The mass number range was 2-720 and 10-3600 at the acceleration voltage of 5000 V and 1000 V, respectively;
- The threshold sensitivity in the test experiments with Ar was $5 \cdot 10^{-5}$ vol. %;
- The resolution value calculated for the 10% peak intensity was better than 1000;
- The ratio error estimated for the mercury isotopes was less than 0.1% at a confidence probability of 95%;
- The ionization voltage of 55 V was chosen to provide the maximal sensitivity. However, some additional runs were carried out at a reduced ionization voltage of 15 V to interpret the pathways of ion generation.

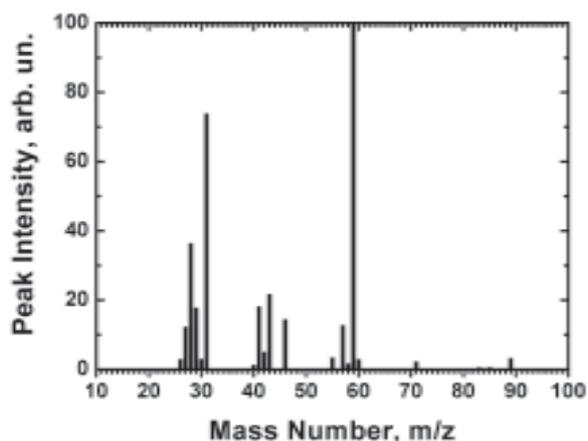


Fig. 2. Typical $\text{Hf}(\text{OBu}^t)_2(\text{mmp})_2$ mass spectrum registered at T_{wall} of 150 °C and P_{tot} of 2 mbar.

3. RESULTS AND DISCUSSION

3. 1. Interpretation of the mass spectrum of undecomposed $\text{Hf}(\text{OBu}^t)_2(\text{mmp})_2$

Fig. 2 demonstrates the mass spectrum of pure $\text{Hf}(\text{OBu}^t)_2(\text{mmp})_2$ registered at 150 °C and 2 mbar. We should emphasize that the effect of the temperature variation from 100 °C to 275 °C on the relative peak intensities of pure $\text{Hf}(\text{OBu}^t)_2(\text{mmp})_2$ spectra was quite negligible; their deviation from the averaged values lies within the limits of a 15% experimental error. Moreover, the main features of the spectra were similar to those observed in the preliminary runs at room temperature. Obviously, the precursor is undecomposed at room temperature, so we believe that it remains stable up to 275 °C. Indeed, possible precursor decomposition should produce additional vapor species, which, in turn, will contribute additional peaks to the mass spectra. Since new peaks were undetectable in these runs and the relative peak intensities remained constant, one can conclude that $\text{Hf}(\text{OBu}^t)_2(\text{mmp})_2$ remained undecomposed. An indirect support for this statement follows also from the fact that the registered mass spectra have much in common with the reference data for organic compounds with a tert-butyl ligand [7]. In particular, the same peaks with m/z of 27, 29, 31, 41, 43, 57, and 59 were identified for tert-butyl hypochlorite and 2-methyl-2-propanol, see Figs. 3a and 3b, respectively. Note that the peak with m/z of 59 is the highest one in the discussed spectra. The pressure effect on the undecomposed $\text{Hf}(\text{OBu}^t)_2(\text{mmp})_2$ spectrum at a given temperature

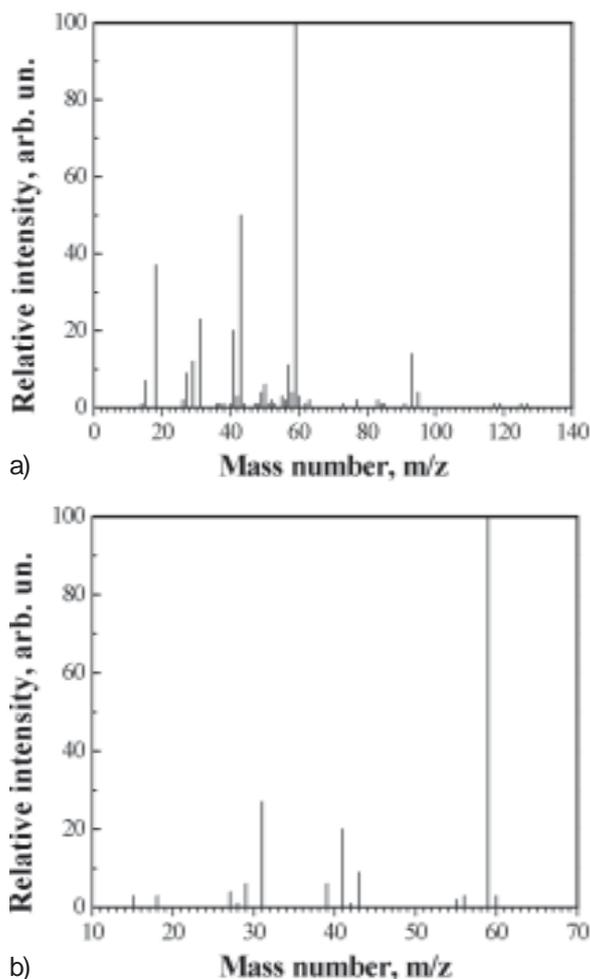


Fig. 3. Typical mass spectra of organic compounds with a tert-butyl ligand; (a) – Tert-Butyl Hypochlorite $[\text{Cl-OC}_4\text{H}_9]$ and (b) – 2-Methyl-2-Propanol $[\text{H-OC}_4\text{H}_9]$, data from [7].

was shown to be insignificant. The absolute peak intensities increased with pressure, while the relative intensities remained constant within the limits of an experimental error.

The results of the mass spectra interpretation are summarized in Table 2. The formation mechanism for the predominant ion with m/z of 59 is hard to explain, since the complex of regrouping processes should be assumed to transform the tert-butyl ligand into an OC_3H_7^+ ion. On the other hand, the formula suggested in Table 2 for this ion is the only possible one. Obviously, the peaks with m/z of 29, 31, 41 and 43 should be attributed to alcoxide groups; a support for this statement follows from the available literature [8,9] and from the modern mass spectrometric databases [7]. The group of peaks with the mass numbers higher than 80 is of special interest for the compound identification. Two

Table 1. Summary on the temperature regimes used in the mass spectrometric study of the Hf(O-Bu^t)₂(mmp)₂ thermal decomposition.

Process	Temperature				Comments
	Ion source region	Ampoule	Input system and mixing volume	Working volume	
	T_{IS}	T_A	T_{MV}	T_{wv}	
Pre-cleaning	200 °C (2 hours at pumping)	25 °C	150 °C (1 hour at pumping)	500 °C (1 hour at pumping)	Before each run at given temperature
Hf(OBu ^t) ₂ (mmp) ₂ measurements	195 °C – ion source, 100 °C – ion source region	60 °C during all run and 100 °C before the precursor flooding	100 °C	50 – 450 °C	T_{MV} was 100 °C at T_{wv} of 50 °C
Cleaning	200 °C (2 hours at pumping)	25 °C	250 °C (6 hours at pumping)	550-600 °C (3 hour at pumping)	Performed after the series of 4-5 runs

Table 2. Possible ions in the Hf(O-Bu^t)₂(mmp)₂ mass spectrum.

M/z	Possible Ion Formulae	M/z	Possible Ion Formulae
26	C ₂ H ₂ ⁺	55	C ₄ H ₇ ⁺ or OC ₃ H ₃ ⁺
27	C ₂ H ₃ ⁺	57	C ₄ H ₉ ⁺ or OC ₃ H ₅ ⁺
28	C ₂ H ₄ ⁺ , CO ⁺	58	OC ₃ H ₆ ⁺
29	C ₂ H ₅ ⁺	59	OC ₃ H ₇ ⁺
30	CH ₂ O ⁺	60	OC ₃ H ₇ ⁺
31	CH ₃ O ⁺	71	OC ₄ H ₇ ⁺
40	C ₃ H ₄ ⁺ or C ₂ O ⁺	82	O ₂ C ₄ H ₂ ⁺ or OC ₅ H ₆ ⁺
41	C ₃ H ₅ ⁺ or C ₂ OH ⁺	83	O ₂ C ₄ H ₃ ⁺ or OC ₅ H ₇ ⁺
42	C ₃ H ₆ ⁺ or C ₂ OH ₂ ⁺	84	O ₂ C ₄ H ₄ ⁺ or OC ₅ H ₈ ⁺
43	C ₃ H ₇ ⁺ or C ₂ OH ₃ ⁺	85	O ₂ C ₄ H ₅ ⁺ or OC ₅ H ₉ ⁺
46	C ₂ H ₆ O ⁺	89	O ₂ C ₄ H ₆ ⁺

pathways of their generation can be suggested. First, it is the formation from the OBU^t (OC₄H₉) ligand. Since the total number of oxygen, carbon, and hydrogen atoms in a single ligand is insufficient to produce these ions (see Table 2); this pathway suggests a complex attachment mechanism between the fragments of two spatially separated ligands. The alternative pathway is the generation of ions from the mmp (OC₄H₈OCH₃) ligand; we believe this mechanism to be more likely than that including the complex of attachment interactions. Thus, the

identification of the peaks with the mass numbers greater than 80 indicates the presence of the mmp ligand in the precursor.

We should emphasize that the molecular peaks, *i.e.* the peaks generated due to the detachment of a single electron from an initial molecule, are usually negligible or even undetectable in most of the available spectra of the organic compounds with the tert-butyl group. Nevertheless, special runs were carried out at a maximal sensitivity to detect hafnium-containing ions. A group of peaks with the

mass numbers lying in range from 528 to 533 were detected at temperatures from 100 to 275 °C. Having been about twice as high as the background signals, these peaks were distinctly observable. However, their relative intensities were negligible, less than 0.002% of the absolute intensity of the maximal peak with m/z of 59. For this reason, the errors in the absolute intensities of hypothetical Hf-containing ions, determined as the difference between the effective and the background intensity, were too high to identify these ions using the Hf isotopic abundance.

3.2. Thermal decomposition of $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ at temperatures above 300 °C

The basic feature of the pure $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ spectrum at temperatures below 275 °C is the constant ratio of the peak intensities. This ratio remained unchanged with temperature for a long time, which was found to be more than 30 minutes at 250 °C. Moreover, the absolute peak intensities were stable within the limit of 10% for that time. Thus, we consider the precursor to be undecomposed here and attribute the absolute intensity deviations as resulting mainly from the variations in the total pressure due to the gas flow-out from the working volume to the mass spectrometer.

In contrast to the above behavior, some traces of time variation were observed in the spectra measured at 300 °C. Just after the precursor flooding, these spectra were similar to those measured at lower temperatures, see Fig. 2. However, the absolute intensity of the peaks attributed to the undecomposed precursor decreased with time. Being within the limits of the experimental error of 10-12 % for the first 8-10 minutes of the run, these deviations became quite observable after a time period of 30 minutes. In addition, some new minor peaks were registered at that moment. We supposed these phenomena to be due to the thermal decomposition of $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$. This assumption was supported by the results of the runs carried out at 400 °C, see Fig. 4. Comparing the registered spectrum with that shown in Fig. 2 as typical for low temperatures, one can see a dramatic difference between them. The peaks with m/z of 44 and 28 are dominant at high temperature, while the relative intensities of the peaks with m/z of 59 and 31 attributed to the undecomposed precursor are less than 5 % here. A lot of new peaks are observed at 400 °C; this fact indicates that the gas contains a

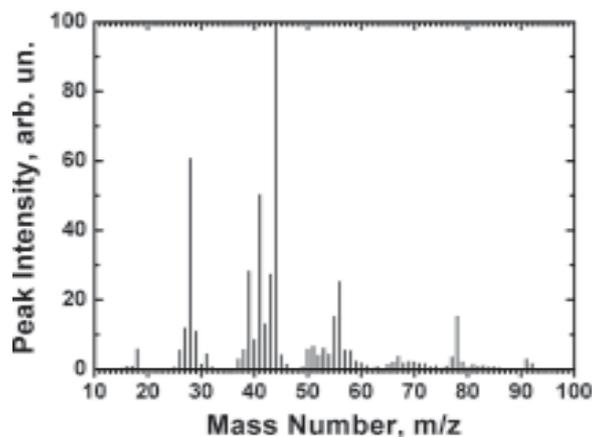


Fig. 4. Mass spectrum registered at $T_{\text{wall}} = 400$ °C.

number of new components generated by the thermal decomposition of the precursor.

Generally, a decomposition rate has a tendency to increase with temperature [10], so it is reasonable to consider the time variations in the mass spectrum at 300 °C to be an indicator of an initial stage of the precursor decomposition. We performed a series of experiments to study this effect. The approach used here can be described as follows. $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ was flooded into the working volume maintained at a given temperature and the time dependence of the absolute intensity of the peak with m/z of 59 (I_{59}^+) was registered. Since this peak was shown to be maximal in the mass spectrum of the undecomposed precursor and additional sources for it were not observed at 400 °C, it seems reasonable to consider the decrease in its absolute intensity as being due to the decrease in the $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ percentage.

As an illustration, Fig. 5 presents the time dependence of I_{59}^+ at 315 °C. Note that I_{59}^+ here is an effective intensity calculated as $I_{59}^+ = I_{59\text{ abs}}^+ - I_{59\text{ final}}^+$, where $I_{59\text{ abs}}^+$ is the measured absolute intensity and $I_{59\text{ final}}^+$ is its residual value [10]. One can see that the decrease in I_{59}^+ is evident at that temperature; it can be well fitted by the exponential decay function. Fig. 6 depicts the experimental $I_{59}^+(t)$ curves registered at the pressure of 1.7 mm Hg for the temperatures 315, 324, 343, and 372 °C (solid lines) and their linear approximations ($\ln(I_{59}^+(t)) = \alpha - \beta t$, dashed lines). It is seen that the linear approximation agrees well with the experimental curves; some discrepancies in the region of small $I_{59}^+(t)$ values should be attributed to large errors inevitable at close values of $I_{59\text{ abs}}^+$ and $I_{59\text{ final}}^+$. Obviously, the coefficient

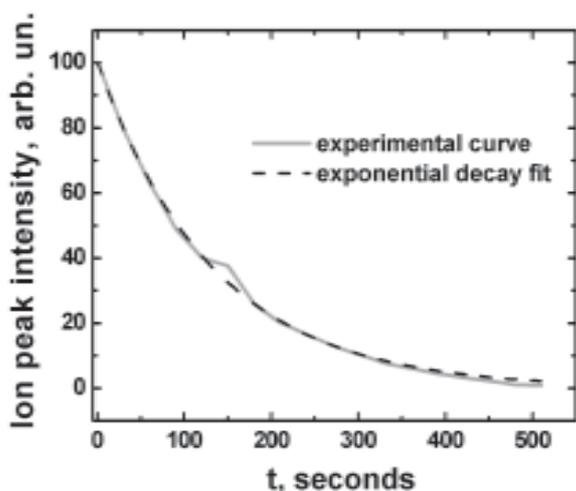


Fig. 5. Time dependence of the absolute intensity of the peak with m/z of 59 ($I_{59}^+(t)$) at 315 °C.

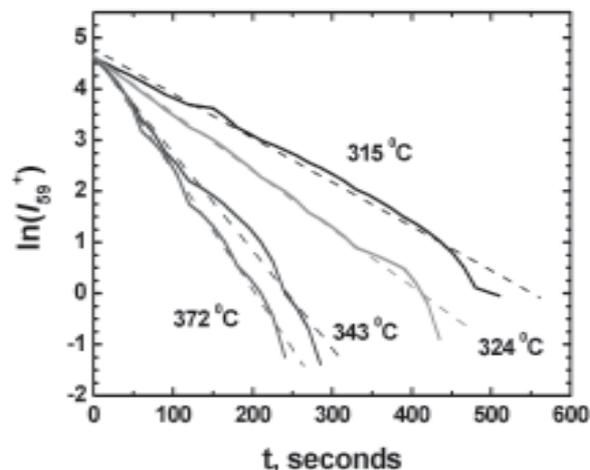


Fig. 6. Time dependencies of $\ln(I_{59}^+)$ at 315, 324, 343, and 372 °C; solid and dashed lines shows the experimental data and their linear fit, respectively.

α in this approximation corresponds to the normalized value of $I_{59}^+(0)=100\%$, while the coefficient β characterizes the temperature behavior.

It follows from the chemical kinetics theory that "...the linear form of the $\lg[A]$ time dependence is the basic criterion to state that the studied process is the first-order reaction" [10], where A is a parameter describing the variations in the reagent percentage. Since the intensity of the ion peak with m/z of 59 was shown above to be proportional to the percentage of undecomposed gaseous $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$, we believe the thermal decomposition of $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ to be a first-order reaction. An additional support for this statement comes from the following consideration. Suppose the equation for the time behavior of the precursor percentage c is

$$\frac{dc}{dt} = -kc^\gamma, \quad (1)$$

where k is a factor responsible for the temperature effect. Obviously,

$$k = \frac{1}{\tau} \frac{1}{(1-\gamma)} (I^{1-\gamma} - I_0^{1-\gamma}) \text{ for } \gamma \neq 1 \quad (2)$$

and

$$k = \frac{1}{\tau} \ln \frac{I_0}{I} \text{ for } \gamma = 1, \quad (3)$$

where $\tau = t - t_0$, $I = I_{59}^+(t)$, and $I_0 = I_{59}^+(t_0)$. Fig. 7 demonstrates the relationship between $\ln(k)$ and the re-

ciprocal temperature for different time moments at a number of γ values. One can see that $\gamma=1$, Fig. 7b, is the only case when the curves for the different time moments are in a good agreement. Values lower or higher than unity give rise to the splitting of a common curve into a number of lines with a similar behavior, see Figs. 7a and 7c. Moreover, the larger is the deviation of the parameter γ from unity, the greater is the curve splitting.

Thus, we conclude that $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ decomposition is a first-order reaction with the kinetic equation $dc/dt = -k(T)c$. In turn, this gives us an opportunity to analyze the temperature behavior of the $k(T)$ function, Fig. 8. It is seen that the curve illustrating the dependence of $\ln k(T)$ vs. the reciprocal temperature $1000/T$ can be considered as consisting of two linear branches. Similar results can be obtained using the approach described in [10]. Indeed, the values of the β coefficient in the equation $\ln(I_{59}^+(t)) = \alpha - \beta t$ for the I_{59}^+ time dependencies, see Fig. 6, fit reasonably well the linear approximation in Fig. 8.

Since the curve branches are fitted linearly, we assume $k(T)$ to be the Arrhenius function

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right), \quad (4)$$

where E_a is the activation energy. Table 3 gives the linear fit coefficients, k_0 and the activation energies calculated from the approximations presented in Fig. 8.

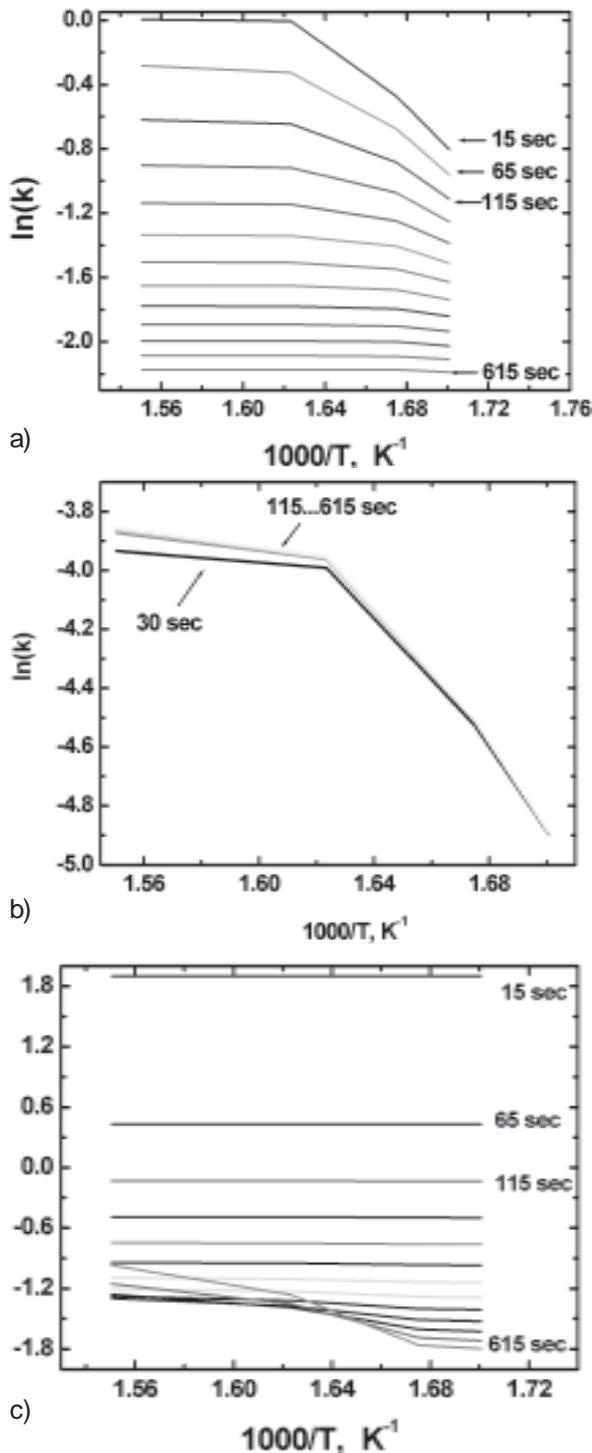


Fig. 7. The relationship between $\ln(k)$ and reciprocal temperature for different time moments at (a) $\gamma=0.1$, (b) $\gamma=1$, and (c) $\gamma=1.5$.

We believe that the branch of the curve corresponding to the temperature range from 300 to 343 °C is attributed to a kinetic regime of the precursor decomposition. In other words, its rate is comparatively low under given operating conditions. There-

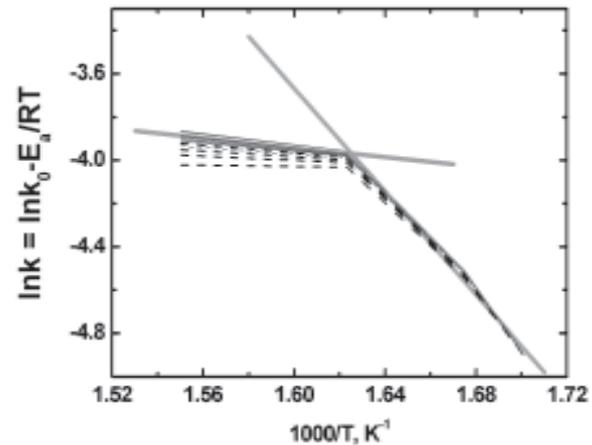


Fig. 8. $\ln(k(T))$ linear approximation; solid lines – linear approximation and dashed lines – experimental data.

fore, the major reason for the variations in the precursor percentage is the $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ decomposition. It is reasonable to assume that the decomposition rate will increase with temperature; nevertheless, the expected tendency is not observed in the temperature range from 343 to 372 °C. This means that an additional mechanism should be accounted for at higher temperatures. We consider some transport limitations to be the reason for this effect. In other words, the expected increase in the decomposition rate has no chance to manifest itself due to the lack of the precursor transported to the hot walls.

Note that the errors in the activation energy and K_0 value are quite acceptable in the temperature range from 300 to 343 °C, while they are too large at high temperatures. This fact also gives an indirect support to the assumption on the effect of an additional mechanism. Therefore, the recommended values marked with (R) in Table 3 are supposed to be fairly applicable for the description of the $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ thermal decomposition in a wide range of pressures and temperatures, while the evaluative values marked with (E) should be used for estimates only due to the fact that their exact values are strictly determined by the given operating conditions.

3.3. Possible mechanisms of $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ thermal decomposition

The pressure-averaged mass spectrum of $\text{Hf}(\text{OBU}^t)_2(\text{mmp})_2$ at 400 °C was presented above in Fig. 4.

Table 3. Linear fit coefficients, k_0 and the activation energies E_a for the Arrhenius function $k(T)=k_0\exp(-E_a/RT)$ used to describe the temperature effect on Hf(OBu^t)₂(mmp)₂ thermal decomposition.

Temperature range	Coefficients* in the linear fit $\ln(k(T)) = \alpha - \beta/T$		K_0 , 1/sec	E_a , kJ/mol	Recommended (R) and Evaluative (E) Values
	α	β			
300-343 °C, approximation of time dependencies in Fig. 8.	15.42±1.7	11930±1010	4.98·10 ⁶	99.2±8.4	(R) $E_a = 92.14±8.4$ kJ/mol
300-343 °C approximation of temperature dependencies in Fig. 6 using the approach [10].	12.66±1.6	10234±930	3.15·10 ⁵	85.1±7.7	(R) $k_0 = 1.25·10^6$ 1/sec
343-372 °C	2.18±0.9	1100±850	8.9	9.1±7.1	$E_a = 15.81±7.1$ kJ/mol (E)

* – A total error including the experimental uncertainties and the errors of previous approximations is presented here.

Runs at higher temperatures of 420 and 450 °C reveal that this spectrum can be considered as a typical one at temperatures above 400 °C. Let us discuss some common features of the high temperature spectra in more detail.

The intensity of the peak with the mass number of 59, attributed to the undecomposed precursor, is small here. Moreover, the intensity ratios of the dominant peaks with m/z of 29, 31, 41, 43 and 45 registered at high temperatures differ from those measured in the range from 100 to 300 °C. For this reason, one can conclude that the percentage of the undecomposed precursor is low at $T > 400$ °C. Since the decomposition rate of Hf(OBu^t)₂(mmp)₂ was shown to be high enough at 400 °C, see Section 3.2, we believe that the complete precursor decomposition occurs at high temperature.

The intensity of the peak with m/z of 44 is found to be the maximal one at high temperature. With respect to the results obtained in the runs carried out at the reduced accelerating voltage of 15 V, we attribute this peak to C₃H₈⁺ and C₂H₄O⁺ ions generated due to the fragmentation of large organic molecules at electron impact. Although the contribution of the molecular CO₂⁺ ion from carbon dioxide should also be accounted for, we believe it to be negligible here because of the oxygen deficiency in

the precursor molecule. Indeed, the preliminary thermodynamic estimates showed that hafnium oxidation should be primarily expected during the Hf(O-Bu^t)₂(mmp)₂ decomposition. This reaction needs two oxygen atoms to produce hafnium dioxide; therefore, four oxygen atoms from each precursor molecule are available for further carbon oxidation. The scheme of this pathway can be written as

$$\text{Hf}(\text{C}_4\text{H}_9\text{O})_2(\text{C}_5\text{H}_{11}\text{O}_2)_2 \rightarrow \text{HfO}_2 + 4\text{O}^* + [\text{hydrocarbon complex}], \quad (5)$$

where O* is an oxygen atom available for the oxidation of the intermediate hydrocarbon complex. Obviously, this pathway can produce only two CO₂ molecules from each precursor molecule. On the other hand, the analysis of the precursor structure shows that process (5) leads to the generation of a large number of small hydrocarbon molecules, and, in turn, to the registration of the peaks with the small mass numbers. However, the peaks with the mass number larger than 58 were detected in the high temperature runs. As seen from Table 2, these peaks should be attributed to oxygen-containing ions. The latter conclusion contradicts the initial assumption that all oxygen atoms are utilized to produce hafnium and carbon oxides. Thus, we consider the contribution of CO₂⁺ ion to the intensity of

the peak with the mass number of 44 as being negligible in the lack of oxygen.

We should emphasize that homogeneous reactions also give rise to the generation of a small hydrocarbon molecules. Indeed, the formation of large complexes within a hypothetical homogeneous pathway should include a number of complex attachment reactions between the spatially separated radicals. On the contrary, heterogeneous reactions on the hot wall seem to be quite a reasonable source of large organic molecules. For this reason, we suppose that the heterogeneous pathway produces large molecules, whereas the homogeneous one gives rise to molecules containing one or two carbon atoms. In terms of the mass spectra, this means that ions with the large mass numbers will be registered during the heterogeneous decomposition. So we conclude that the identification of ions with the mass numbers larger than 58 in the high temperature Hf(OBu)₂(mmp)₂ spectrum is an indirect support for the heterogeneous decomposition pathway. On the other hand, the effect of transport limitations, see Section 3.2, indicates the possibility of homogeneous decomposition as an alternative pathway. A set of special runs at extremely reduced pressures was carried out to separate heterogeneous effects from homogeneous ones; the results indicated that the heterogeneous mechanism of the Hf(OBu)₂(mmp)₂ thermal decomposition seems to be more likely at high temperatures.

4. CONCLUSIONS

Mass spectrometric study of the Hf(OBu)^t₂(mmp)₂ thermal decomposition have been carried out in the temperature range from 100 to 450 °C at pressure varied from 0.5 to 5 Torr. The analysis of the experimental results can be summarized as follows.

- Hf(OBu)^t₂(mmp)₂ remains stable at temperatures below 275 °C. Mass spectra are pressure-independent; in other words, an increase in the total pressure leads to an increase in the absolute intensities of the peaks, while their relative intensities remain constant. The same set of peaks was registered in the whole temperature range, indicating that decomposition products are absent from the gas;
- The analysis of the mass spectra has shown that the detected peaks are typical for organic compounds with tert-butyl ligands. Peaks with the mass numbers larger than 80 are attributed to the mmp group. A set of experiments at reduced ionization energy of 15 V supports the above interpretation;

- We have registered peaks with mass numbers similar to those expected for Hf-containing molecular ions. Since their absolute intensities were extremely low, we failed to verify their origin using the approaches based on the reduction in the ionization energy and on the isotopic abundance of pure hafnium.
- The onset of Hf(OBu)^t₂(mmp)₂ thermal decomposition was found to occur at temperatures above 300 °C; a kinetic regime of decomposition was observed at temperatures from 300 to ~340-350 °C. An additional mechanism manifests itself at higher temperatures; we believe this effect to be due to some transport limitations;
- Hf(OBu)^t₂(mmp)₂ decomposition has been shown to be a first-order reaction;
- The Arrhenius function $k(T) = k_0 \exp(-E_a/RT)$ is proposed to describe the temperature effect on the precursor decomposition, the activation energy E_a of 92.14 kJ/mol and k_0 of $1.25 \cdot 10^6$ 1/s are recommended for the temperature range up to 350 °C at a pressure varying from 0.5 to 5 mm Hg;
- A complete Hf(O-But)₂(mmp)₂ decomposition was observed above 400 °C. It occurs due to heterogeneous reactions on the hot wall; however, the contribution of the homogeneous pathway should also be accounted for.

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