

Mass spectrometric study of the thermal decomposition mechanism of vapors of 2,2,6,6-tetramethyl-3-iminoheptane-5-one and its copper(II) complex

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Abstract

Thermal conversions of vapors of ketoimine $C(CH_3)_3C(NH)CH_2C(O)C(CH_3)_3$ (Htmha = 2,2,6,6-tetramethyl-3-iminoheptane-5-one) and its chelate coordination compound with copper $Cu(tmha)_2$ is studied by in situ mass spectrometry in a vacuum and in the presence of hydrogen. Experiments are carried out under conditions close to low pressure chemical vapor deposition at the evaporator temperature of 130 °C and the reactor temperature range 130–500 °C. It is found that compounds are monomeric in the gas phase. Based on temperature dependences of the composition of primary gaseous products, the mechanism of thermal decomposition is proposed. The decomposition of ketoimine on the heated surface begins at 350 ± 10 °C and proceeds by the elimination of terminal groups. Its copper complex decomposes in two directions and yields both molecular and radical products. The latter provide the assumption that metallic copper forms as the only one solid product. The results obtained are compared with those for copper dipivaloylmethanate(2,2,6,6-tetramethylheptane-3,5-dionate).

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1. Introduction

A successful development of various technologies using metal complexes with organic ligands in order to obtain diverse materials requires understanding the mechanism of the underlying chemical transformations. In particular, for chemical vapour deposition (CVD) [1] that applies volatile organometallic complexes, the chemical aspects, such as adsorption, activation, conversion of the complex molecules on the surface, become decisive in the selection of starting compounds and deposition conditions. Owing to rapidity and relative simplicity in interpreting the experimental data, different mass spectrometric techniques have

found a rather wide application for investigating the mechanism of chemical conversions.

The mechanism of thermal conversions of the organometallic compound has been studied by mass spectrometry on both relatively simple compounds, for example, examinations of aluminum alkoxides [2,3] or silver(I) tri-*n*-butylphosphine complexes [4], and more complex such as metal β -diketonates [5–7]. The authors of the present paper have much experience in applying mass spectrometry to the investigation of these complexes [8–11]. The peculiarity of these investigations is the use of the input system for mass spectrometer that imitates the CVD reactor. Only the vapors of the initial compound are supplied to such a reactor; thermal conversions take place on the surface, whereas the reaction mixture flows into the mass analyzer through the effusion hole in the reactor. Thus, the possibility of analyzing the gas phase composition almost in situ avoiding probable secondary reactions is achieved.

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Our present study was inspired by the perspectives of using volatile metal β -ketoiminates as precursors for depositing pure metal films due to a lower content of oxygen, giving some advantage to these compounds over metal β -diketonates. Furthermore, metal β -ketoiminates and β -diketonates possessing the same substituents have similar volatility [12].

Coordination chemistry of bidentate ketoiminate ligands containing *N*, *O* donor atoms are well known [13]. Along with β -diketonates, these ligands have been used to prepare volatile complexes of main group elements, lanthanides and transition metals for CVD applications to obtain metal and oxide films [14–20].

Perhaps, the only one article devoted to the investigation of thermal behavior and decomposition of ketoiminate vapors is the work on dimethylgold ketoiminates [21]. The authors present the results of the systematic study of a series of dimethylgold ketoiminates in the gas and condensed phases.

The focus of the study reported here is the revelation of the mechanism of decomposition of copper(II) 2,2,6,6-tetramethyl-3-iminoheptane-5-onate $\text{Cu}(\text{tmha})_2$ vapors. Thermal conversions of the compound vapor on the heated surface were studied in a vacuum and in the presence of hydrogen using a mass spectrometric technique. Decomposition of free Htmha ligand vapor is also studied to clearly understand the decomposition of the copper compound.

It should be noted that because ketoiminate is difficult for the investigation being a system of many different atoms, here we speak not about the study of the mechanism at the level of elementary acts, but about the identification of the reaction products, possible ways of their formation, and temperature ranges of the process. Such a qualitative approach provides the possibility of estimating the composition of the vapor of the initial complex and its vaporization stability and of predicting the composition of the solid phase in the decomposition of vapors on the surface [22,23].

We have described the synthesis and characterization of the compounds studied here in [24]. The compounds were preliminarily purified by sublimation. The data obtained are specially compared with those previously reported on the thermal behavior of 2,2,6,6-tetramethylheptane-3,5-dione Htmhd and their copper(II) complex $\text{Cu}(\text{tmhd})_2$ [25].

2. Results and discussion

2.1. Mass spectrum of the compounds

The fragmentation of the ligand under electron impact is similar to that for Htmhd and mainly proceeds by eliminating one terminal C_4H_9 group with the formation of the ion peak at m/z 126 (Table 1).

For the copper complex, there are no peaks in mass spectra with m/z exceeding the molecular ion mass (427 a.m.u. for $^{63}\text{Cu}(\text{tmha})_2$) indicating that the compound

Table 1
Mass spectra of Htmha and dipivaloylmethane Htmhd and their copper(II) complexes (EI, ionization energy – 70 eV)

| Ion, ^a R = C ₄ H ₉ | <i>m/z</i> | Relative intensity (%) | | <i>m/z</i> | Relative intensity (%) [22] | |
|---|------------|------------------------|--------------|------------|-----------------------------|--------------|
| | | CuL ₂ | HL, L = tmha | | CuL ₂ | HL, L = tmhd |
| [CuL ₂] ⁺ | 427 | 78 | – | 429 | 12 | – |
| [CuL ₂ –R] ⁺ | | 12 | – | 373 | 25 | – |
| [CuL ₂ –2R] ⁺ | 313 | 59 | – | 315 | 53 | – |
| [CuHL] ⁺ | 246 | 16 | – | 247 | 8.5 | – |
| [CuL–R] ⁺ | 188 | 30 | – | 189 | 19 | – |
| [HL] ⁺ | 183 | 13 | 18 | 184 | 11 | 9 |
| [HL–2R] ⁺ | 126 | 90 | 100 | 127 | 100 | 100 |
| | 110 | 7 | 8 | | | |
| | 96 | | 8 | 109 | 8 | 11 |
| | 83 | 10 | 8 | 85 | | 13 |
| | 81 | 8 | 7 | 81 | 18 | 10 |
| [N≡CCH ₂ CHO] ⁺ | 69 | 10 | 5 | 69 | 10 | 6 |
| | 68 | 12 | 7 | | | |
| [C ₄ H ₉] ⁺ | 57 | 100 | 26 | 57 | 52 | 50 |
| | 55 | 25 | 14 | | | |
| [CH ₃ CO] ⁺ | 43 | 17 | 8 | 43 | 80 | 58 |
| | 42 | 22 | 17 | | | |
| [C ₃ H ₅] ⁺ | 41 | 84 | 40 | 41 | 19 | 25 |
| [C ₃ H ₃] ⁺ | 39 | 37 | 21 | 39 | | 13 |
| [C ₂ H ₅] ⁺ | 29 | 55 | 24 | 29 | 17 | |
| | 28 | 24 | 14 | | | |
| [C ₂ H ₃] ⁺ | 27 | 31 | 17 | 27 | | |
| [CH ₃] ⁺ | 15 | 15 | 12 | 15 | | |

^a Here copper-containing ions are presented as the most occurring isotope ^{63}Cu .

is monomeric in the gas phase. The fragmentation path under electron impact with the elimination of terminal groups of the ligand is typical of copper β -diketonates [11,26]. The 100% intensity of the molecular ion among copper-containing peaks should be noted, while for copper(II) dipivaloylmethane $\text{Cu}(\text{tmhd})_2$ the intensity of the molecular ion is low and the most intensive is $[\text{Cu}(\text{tmhd})_2-2\text{C}_4\text{H}_9]^+$ with m/z 315 (Table 1). Evidently, the presence of the imino-group makes the molecular ion more stable for the copper complex. As well as for the majority of metal complexes with non-fluorinated β -diketonates, there are peaks corresponding to free ligand Htmha and products of its fragmentation.

2.2. Thermal decomposition study

New peaks are not observed in the mass spectra recorded under heating the vapors of the titled compounds; only a change in the intensity is observed. It means that products upon thermal decomposition and electron impact ionization are the same. In other words, ions with the same m/z form both upon the fragmentation of the molecular ion of the initial compound and ionization of thermal decomposition products under electron impact. However, it is possible to separate these two paths by analyzing the thermal dependence of the mass spectra because the intensity of the ion peaks changes when the vapor of compounds is heated. In mass spectrum intensity of fragmentary ion peak is constant value with respect to intensity of the parent ion, thus curve of temperature dependence of fragmentary ion peak has the same shape as that one for parent ion. Difference in this shape indicates that such a fragmentary ion originates from two (or more) parent particles and separation of the integral curve is carried out if necessary.

Figs. 1–3 display the temperature dependences of the intensity of ions peaks in the mass spectrum characterizing the gas phase composition.

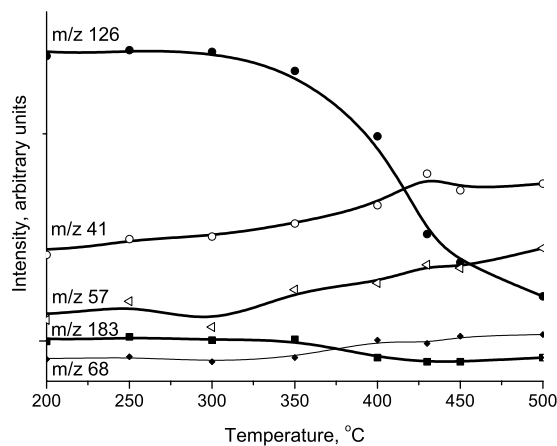


Fig. 1. Temperature dependence of intensity of the main peaks in the mass spectrum characterizing gas phase composition upon Htmha thermolysis.

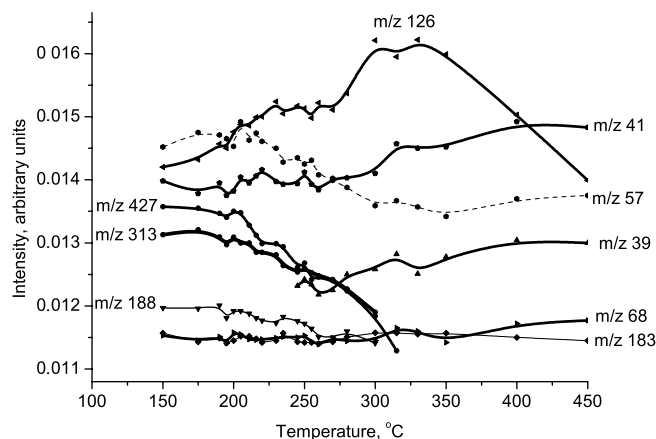


Fig. 2. Temperature dependence of intensity of the main peaks in the mass spectrum characterizing gas phase composition upon $\text{Cu}(\text{tmha})_2$ thermolysis in vacuum.

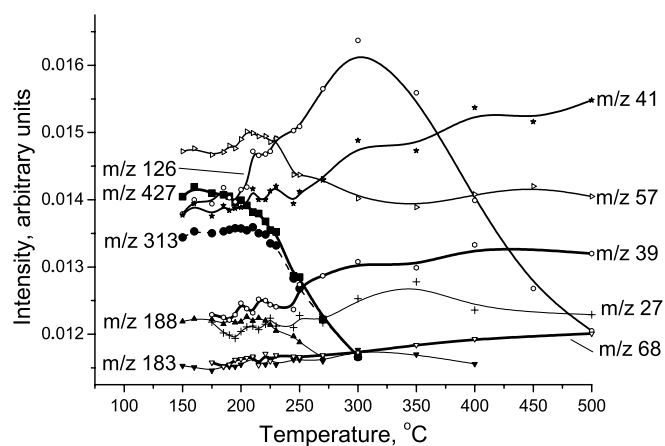
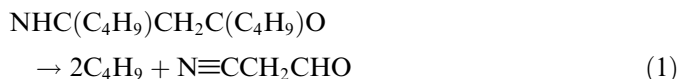


Fig. 3. Temperature dependence of intensity of the main peaks in the mass spectrum characterizing gas phase composition upon $\text{Cu}(\text{tmha})_2$ thermolysis in the hydrogen presence.

2.2.1. Thermal decomposition of Htmha vapours

The temperature dependence of the gas phase composition (Fig. 1) was used to evaluate thermal stability. A decomposition onset temperature was determined as the temperature when a decrease in the molecular peak intensity is observed in the mass spectrum simultaneously with an increase in the intensity of the products peaks. In a vacuum it occurs at 350 ± 10 °C. According to Ref. [25], the decomposition of dipivaloylmethane Htmhd starts at 590 ± 10 °C. Therefore, it could be concluded that substitution of keto-group for imino-group results in a considerable decrease in thermal stability.

The products of decomposition are recorded in the mass spectrum as peaks at m/z 57 (with the fragmentary ions at m/z 41, 29) for C_4H_9 and 69 (with the fragmentary 68) for $\text{N}\equiv\text{CCH}_2\text{CHO}$. Following the composition of gaseous products, the heterogeneous decomposition of Htmha proceeds through elimination of two *tert*-butyl groups and finally can be presented by Eq. (1)



Note that this simple way differs from that one for dipivaloylmethane which decomposes with the abstraction of H_2O to produce $\text{C}_4\text{H}_9\text{C}(\text{O})\text{C}\equiv\text{CC}_4\text{H}_9$ [25].

2.2.2. Thermal decomposition of $\text{Cu}(\text{tmha})_2$ vapours

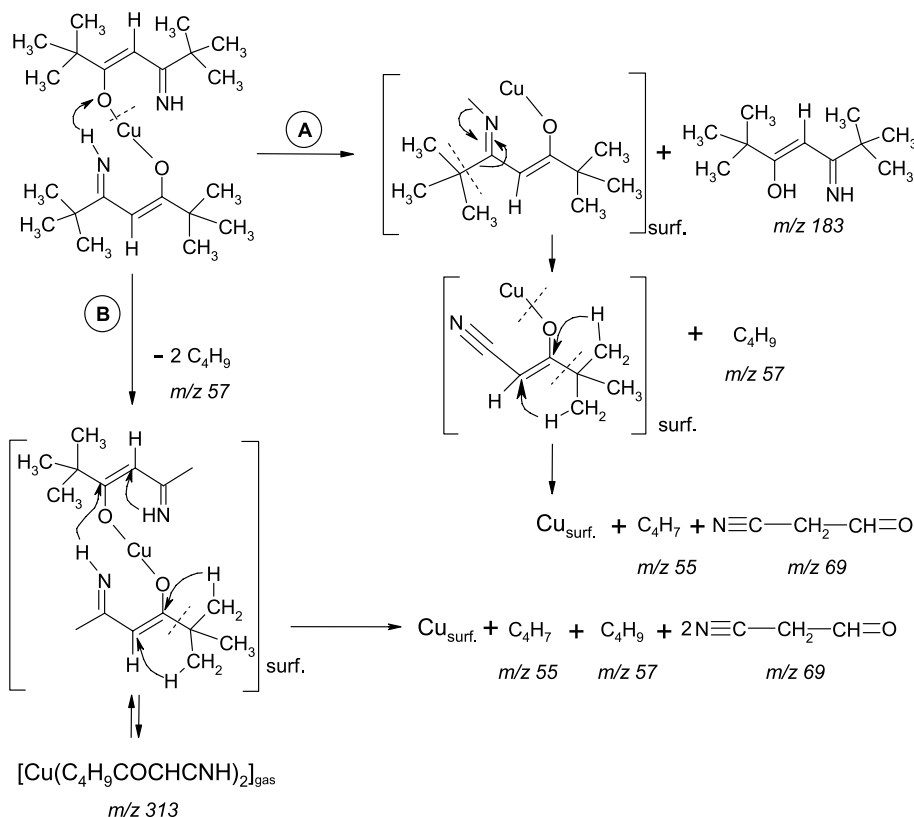
The copper complex has sufficient vaporisation stability at least up to 150°C that is confirmed by the fact that there are no changes in the mass spectrum under repeated heating and cooling cycles of the evaporator.

To study thermal conversions, the compound vapor incoming from the evaporator was heated in the reactor from 150 to 500°C in a vacuum and in the presence of hydrogen. Several repeated experiments have been made with the same heating and cooling rate. The mass spectra are recovered completely after cooling the reactor and the composition of products does not change in subsequent experiments.

Fig. 2 displays the temperature dependences of ion peaks of the mass spectrum recorded in a vacuum and hydrogen presence. The form of these curves merits our special consideration. In a vacuum, the intensity of copper-containing peaks starts to decrease at a temperature above 200°C and reaches the background level at 300°C . Note that these curves are mildly sloping – there is no characteristic pronounced reduction of the intensity after the

onset temperature. The described trend is kept in the presence of hydrogen, though the curves have a sharper slope. Also we were astonished at unusual behavior of the curves corresponding to the peaks of the molecular ion $[\text{Cu}(\text{tmha})_2]^+$ and $[\text{Cu}(\text{tmha})_2-2\text{R}]^+$ ($\text{R} = \text{C}_4\text{H}_9$) ion. With the temperature rising, the intensity of $[\text{Cu}(\text{tmha})_2-2\text{R}]^+$ does not decrease in parallel with the molecular ion $[\text{Cu}(\text{tmha})_2]^+$, and at a temperature above 250°C its intensity becomes higher than the intensity of the molecular ion. It occurs on the background of the gradual growth of the intensity of peaks for decomposition products. This feature was well reproduced from one experiment to another. Earlier, the authors have investigated quite a number of metal β -diketonates including the complexes of copper(II) [11,26]. Unlike other complexes, the compound under investigation shows distinct behavior of metal-containing peaks when heated. Such a behavior of $[\text{Cu}(\text{tmha})_2-2\text{R}]^+$ may be explained by that its parent particle forms in the decomposition of the initial compound on the surface and then it desorbs in a gas phase that enables its record in the mass spectra.

Apart from the above particle, the following peaks corresponding to reaction products are observed in the mass spectrum: free ligand Htmha at m/z 183 (with the most intensive fragmentary ion at m/z 126), *tert*-butyl-radical C_4H_9 at m/z 57 and C_4H_7 at m/z 55, $\text{N}\equiv\text{CCH}_2\text{CHO}$ at m/z 69 with a more intensive fragmentary ion at m/z 68. It should be also noted that free ligand is a typical



Scheme 1. Mechanism of decomposition of the investigated complex on heated surface.

decomposition product for non-fluorinated metal β -diketonates, and in particular for copper(II) complexes [22,23]. Gaseous products of decomposition in a vacuum are similar to those formed in the presence of hydrogen.

Based on the revealed composition of gaseous products, we assume the following mechanism of decomposition of the investigated complex on the heated surface (Scheme 1). The process of free ligand formation (A) is the result of an intramolecular proton transfer from one ligand to another with the breakage of one Cu–O bond. It occurs in parallel with the elimination of *tert*-butyl groups (B) and a number of rearrangements leading to the particle recorded in the mass spectrum as $[\text{Cu}(\text{tmha})_2-2\text{R}]^+$ ion. Further both ways result in that C_4H_9 , C_4H_7 radical particles and the $\text{N}\equiv\text{CCH}_2\text{CHO}$ molecular product (m/z 69) escape to the gas phase. Despite the presence of identical products, we exclude the possibility of formation of the particle with m/z 69 owing to thermolysis of the formed ketoimine upon the decomposition of copper(II) ketoiminate. The study of ketoimine thermolysis performed shows that this process occurs in another temperature interval and decomposition begins at a temperature higher by 50° .

From the composition of gaseous products of thermal decomposition that is suggested based on the analysis of the temperature dependence it follows that the main solid product is metallic copper (as a film on the walls of the reactor). Moreover, the formation of exactly metallic copper in the solid phase is indirectly confirmed by the following. Peaks of the particles similar to $\text{RC}\equiv\text{CC}(\text{O})\text{R}$, $\text{RCH}=\text{CHC}(\text{O})\text{R}$ are absent in the mass spectrum, while they indicate the breakage of the C–O bond in the ligand, as it was shown in the case of copper and lead dipivaloylmethanates. It is this bond breakage that results in the formation of a metal oxide in the solid phase [22,25]. It should be added that copper films have been prepared by CVD from the investigated copper complex in the predicted temperature range and the results will be reported later in separate paper.

The comparison with β -diketonates shows that the studied complex with ketoiminate and copper is less thermally stable than dipivaloylmethanate whose decomposition starts at 330°C . As for the compound studied, the degree of its decomposition reaches its maximum at 300°C , which is indicated by a high intensity of the peaks of reaction products and almost the background intensity of the peaks of the initial compound. Note that $\text{Cu}(\text{tmha})_2$ when heated in the condensed phase is less stable than $\text{Cu}(\text{tmhd})_2$ [24].

3. Conclusions

Having investigated the mechanism of the thermal decomposition of vapors of compounds on the surface, we state that the decomposition of ketoimine proceeds in one stage with the elimination of terminal groups. The decomposition of its complex with copper occurs in two directions and leads to the formation of both molecular and radical products. They provide the assumption that

metallic copper forms as the only one solid product. Both compounds described possess sufficient storage and vaporization stability. A relatively low temperature of decomposition and a smaller oxygen content in comparison with β -diketonate makes the copper(II) complex a promising precursor for the deposition of pure (oxygen-free) copper films.

Apart from the data on the mechanism of thermal decomposition which develop our ideas of the chemistry of organometallic compounds, we obtain valuable information for the practical application. In particular, we again demonstrate the possibility of making an assumption on the composition of the solid product of decomposition based on the analysis of primary gaseous product. The technological aspect of the study performed is to test various volatile organometallic compounds for their applicability in CVD processes. A doubtless advantage of this is the use of small amounts of the initial substance and avoidance of the tedious routine search for the temperature range.

To develop the study performed and confirm its conclusions about the solid phase composition, it is expected to continue the experiments and obtain copper films from the compound in question. The data on the temperature ranges obtained at that we will use to find the deposition conditions.

4. Experimental

The thermal decomposition of the compound vapours was studied by the mass spectrometric technique which is the combination of Knudsen effusion method with mass spectrometric measurements of the gas phase composition [27]. The experimental details are described in Ref. [11]. The compound (about 5 mg) in a glass ampoule was heated in the evaporator to 85°C for Htmha and 130°C for $\text{Cu}(\text{tmha})_2$, respectively. Evaporator temperature kept constant and vapors of the initial compound supplied to the reactor through a heated pipeline. During the experiment, the reactor temperature was changed from the above temperature to 500°C with a heating rate of 5 degrees per minute. The reaction mixture flows through the effusion hole (0.2 mm) from the reactor into the mass analyzer of the mass spectrometer. It should be noted that vapors only were heated in the reactor and the experiment conditions were as such that decomposition occurred on the walls of the reactor. Working pressure changed within the order of 10^{-6} Torr magnitude, while vapor pressure of the compound was not higher than 10^{-3} Torr). The fast recording of the gas phase composition was carried out: the time from the moment when a particle left the reactor to the moment when it is recorded did not exceed a millisecond. This enables us to record primary gaseous decomposition products in situ, as well as to measure the temperature ranges in which they form. The reagent gas (hydrogen) is introduced directly into the reactor.

Mass spectra were recorded at the energy of ionizing electrons of ≈ 70 eV with a time-of-flight mass spectrometer. In

preliminary experiments screening of all available mass range (3000 a.m.u.) at ionization energy 10–100 eV was carried out.

The automated system for data recording and processing based on *National Instruments Corp.* hardware was used. Temperature dependences of the gas phase composition were produced from the mass spectra at different temperatures.

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