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The thermal decomposition of copper(II) and lead(II) pivaloyltrifluoracetonates by high-temperature mass spectrometry

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Abstract

The thermal behaviour of copper(II) and lead(II) pivaloyltrifluoracetonates (2,2-dimethyl-6,6,6-trifluoro-3,5-hexanedionates) have been studied by high-temperature mass spectrometry in vacuo and in the presence of various added gases (oxygen, hydrogen). The initial decomposition temperatures and composition of primary gas products have been determined. Thermolysis mechanisms of copper and lead pivaloyltrifluoracetonates have been proposed and common thermal decomposition mechanisms of these complexes are evident. © 1997 Elsevier Science B.V.

Keywords: Copper(II) pivaloyltrifluoracetonate; Decomposition; β-Diketonate; Lead(II) pivaloyltrifluoracetonate; Mass spectrometry; Thermolysis mechanism

1. Introduction

The characteristics of volatility, high thermal stability in the condensed state and in the gas phase and stability in air promote the use of metal β-diketonates in chemical vapour deposition (CVD) processes. In particular, copper(II) β-diketonates are used in the production of superconducting oxide films and to metallize superlarge integrated schemes. At present, volatile lead(II) β-diketonates are used in gas-phase processes to obtain functional oxide films and coatings. For the purpose of preparing films and coatings and maintaining their properties, it is necessary to study the thermal behaviour of the vapours of the component materials.

The present work is a continuation of a systematic investigation of the thermal behaviour of metal complexes of various β-diketones in the gas phase within the framework of high-temperature mass spectrometry [1–10]. The present study is an investigation of the thermal behaviour of copper and lead complexes of pivaloyltrifluoracetone '$M(pta)_2$', where pta = $CF_3COCHCOC(CH_3)_3$, M = Cu, Pb.

2. Experimental

The experimental technique has been described previously [11].

Experimental data have been presented in the form of temperature dependences of ion peak intensities of the compound and its thermal decomposition products in vacuo and in the presence of oxygen or hydrogen. To eliminate the influence of the reactor material and for the purpose of obtaining reproducible results, the surface of thermal reactor has been prepared prior to

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the experiment by passing the vapour of the corresponding complex for 3-4 h through the reactor heated to 550°C.

Experimental conditions have been chosen so that the thermal decomposition of the vapour of compounds, under investigation, occurred on the surface of thermal reactor and not in the gas phase, since the free path length of molecules is much longer than the linear size of the reactor. Because of this, the occurrence of secondary reactions between the molecules of compounds under investigation and the products formed are negligible, and the obtained data on the composition of gaseous decomposition products are related to primary products.

The temperatures in the vapourization zone and the corresponding vapour pressures are calculated from the data reported in Refs. [12,13] and the thermolysis temperature intervals are as follows:

$Cu(pta)_2$	80°C,	12.7 Pa	190–640°C
$Pb(pta)_2$	153°C,	25.3 Pa	200–600°C.

Initial compounds were synthesized according to standard procedures [14,15] and purified twice by vacuum sublimation.

3. Results

3.1. Mass spectra data

Mass spectra of the complexes were recorded at the energy of ionizing electrons of approx. 70 eV. The spectra exhibited a large set of the peaks related to metal-containing ions (Figs. 1 and 2). In all cases, a peak with the largest mass to charge ratio (*m/z*) corresponded to the molecular ion $[M(pta)_2]^+$ indicates a monomeric composition of the vapour.

Fragmentation of molecular ions of the complexes caused by electron impact proceeds via two main routes, namely, the formation of $[M(pta)]^+$ (pta is deprotonated form of pivaloylfluoracetone) and its further fragmentation and consequent abstraction of terminal substituents of ligands from the molecular ion.

It is also noteworthy that the peak related to the molecular ion of the β-diketone is present in the mass spectra of the parent complexes.

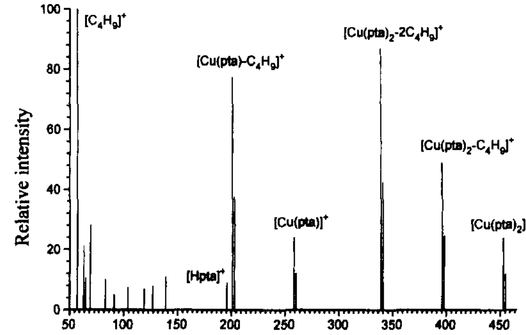

Fig. 1. Electron impact (70 eV) mass spectrum of copper pivaloylacetonate $Cu(pta)_2$.

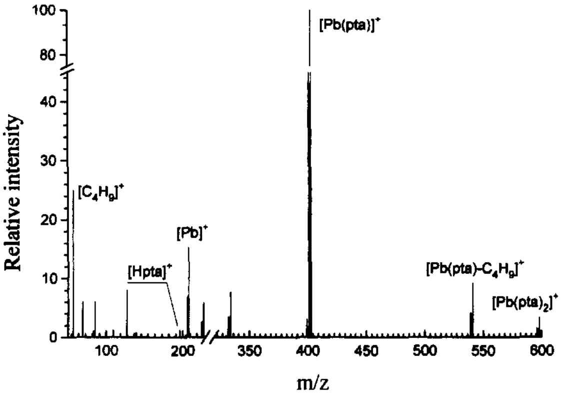

Fig. 2. Electron impact (70 eV) mass spectrum of lead pivaloylacetonate $Pb(pta)_2$.

3.2. Thermal decomposition of copper pivaloyltrifluoracetonate $Cu(pta)_2$ in vacuo, in hydrogen and in oxygen

Temperature dependence of the intensity of peaks in the mass spectra corresponding to gaseous products of $Cu(pta)_2$ thermolysis are shown in Figs. 3–5, respectively. Data on thermal stability are presented in Table 1. We used the temperature of the commencement of decomposition as a measure of thermal stability of the complexes. The initial temperature of decomposition (or threshold temperature) was taken to be equal to the temperature at which a sharp decrease of the intensity of molecular ion peak was observed [16]. The composition of gaseous products of complex decomposition in the presence of added gases is

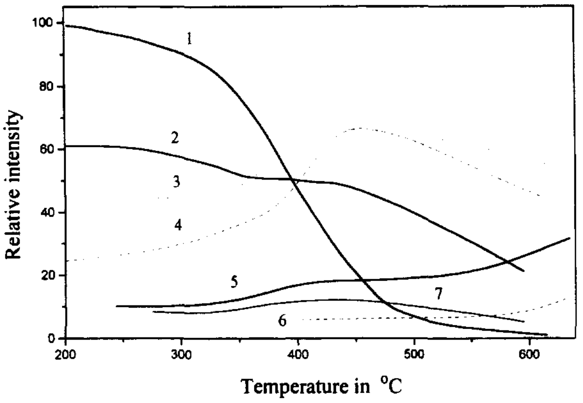

Fig. 3. Temperature dependence of intensity of ion peaks characterized the gas-phase composition upon thermolysis of $Cu(pta)_2$ in vacuo: 1 – $[Cu(CF_3C(O)CHCO)]^+$; 2 – $[C_4H_9]^+$ (1 : 2); 3 – $[CHCO]^+$; 4 – $[CF_3]^+$; 5 – $[CO]^+$; 6 – $[Hpta]^+$; 7 – $[HF]^+$.

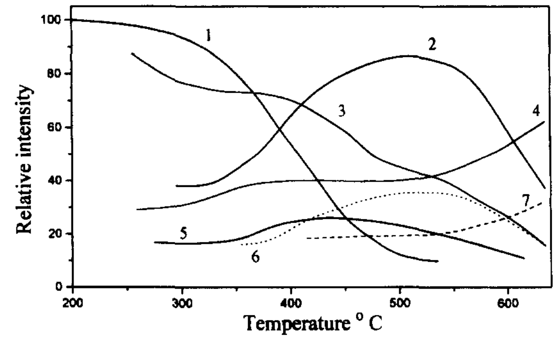

Fig. 4. Temperature dependence of intensity of ion peaks characterized the gas-phase composition upon thermolysis of $Cu(pta)_2$ in hydrogen: 1 – $[Cu(pta)_2]^+$; 2 – $[C_4H_9]^+$ (1 : 4); 3 – $[CF_3]^+$ (1 : 2); 4 – $[CO]^+$; 5 – $[Hpta]^+$; 6 – $[CHCO]^+$ (1 : 2); 7 – $[HF]^+$.

similar to that observed in vacuo. Molecular products (pivaloyltrifluoracetone Hpta, CO, HF) are observed together with radicals ($C(CH_3)_3$, CF_3, CHCO). It should be noted that among the studied fluorine-containing copper β-diketonate complexes only $Cu(pta)_2$ forms a small amount of free ligand Hpta during thermal decomposition. Figs. 3 and 4 show that temperature dependence of $[C(CH_3)_3]^+$ ion peak is stepwise. This is explained by the formation of this ion during fragmentation of both the initial complex and the products of its decomposition. For example, below the threshold temperature, the registered ions are formed mainly as a result of fragmentation of $Cu(pta)_2$, while above this temperature they are formed by fragmentation of the products of complex decomposition, in particular, pivaloyltrifluoracetone. The shape of the temperature dependence curve for the $[CO]^+$ peak intensity indicates the formation of carbon monoxide at several stages of thermolysis.

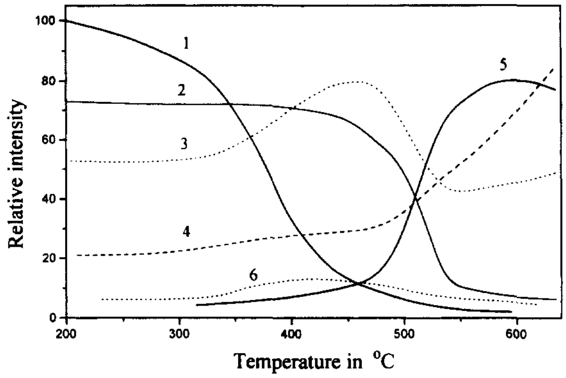

Fig. 5. Temperature dependence of intensity of ion peaks characterized the gas-phase composition upon thermolysis of $Cu(pta)_2$ in oxygen: 1 – $[Cu(CF_3C(O)CHCO)]^+$; 2 – $[O_2]^+$ (1 : 3); 3 – $[CHCO]^+$; 4 – $[CO]^+$ (1 : 2); 5 – $[CO_2]^+$ (1 : 4); 6 – $[Hpta]^+$.

Table 1
Thermal decomposition data

	Threshold decomposition temperatures, T ± 10°C		
Compound	Vacuo	Hydrogen	Oxygen
$Cu(pta)_2$	345	335	330
$Pb(pta)_2$	380	—	300

At temperatures higher than 490°C, the intensity of metal-containing peaks is close to zero which indicates that the initial compound is decomposed completely within this temperature range.

The intensity of $[O_2]^+$ peak starts decreasing at higher temperatures than the threshold temperature of complex decomposition, which indicates that oxygen reacts only with the products of the reaction (at $T > 460°C$), as is the case with other complexes. Substantial amounts of CO, CO_2, H_2O are formed in this process.

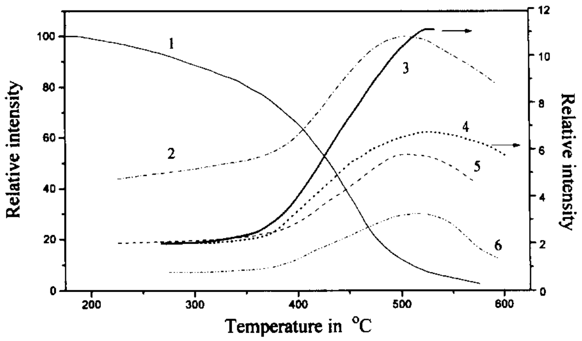

Fig. 6. Temperature dependence of intensity of ion peaks characterized the gas-phase composition upon thermolysis of $Pb(pta)_2$ in vacuo: 1 – $[Pb(pta)]^+$; 2 – $[C_4H_9]^+$; 3 – $[CO]^+$; 4 – $[Hpta]^+$; 5 – $[CHCO]^+$, 6 – $[CF_3]^+$.

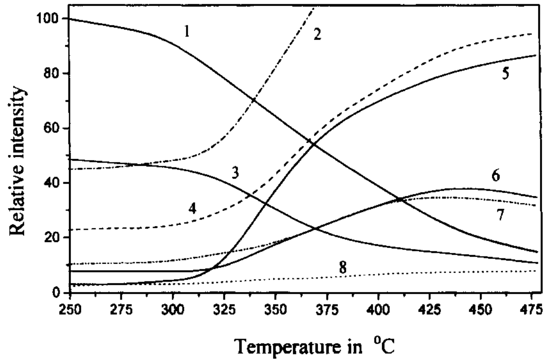

Fig. 7. Temperature dependence of intensity of ion peaks characterized the gas-phase composition upon thermolysis of $Pb(pta)_2$ in oxygen: 1 – $[Pb(pta)]^+$; 2 – $[C_4H_9]^+$; 3 – $[O_2]^+$; 4 – $[CHCO]^+$; 5 – $[CO_2]^+$; 6 – $[CO]^+$; 7 – $[CF_3]^+$; 8 – $[Hpta]^+$.

3.3. Thermal decomposition of lead pivaloyltrifluoracetonate $Pb(pta)_2$ in vacuo and in oxygen

Temperature dependence of the intensities of peaks in the mass spectra corresponding to gaseous products of $Pb(pta)_2$ decomposition in vacuo are shown in Fig. 6. The initial complex (see Figs. 6 and 7) is presented by the $[Pbpta]^+$ peak, since all other metal-containing peaks exhibit similar behaviour, as for $Cu(pta)_2$. The absence of intensity disproportionation with temperature increase indicates that metal-containing ions are not formed during thermal decomposition. Among the products, are both molecular (Hpta, CO) and radicals (CF_3, CHCO, $C(CH_3)_3$).

At temperatures higher than 550°C, intensities of metal-containing peaks are close to zero, which indicates complete complex decomposition.

Thermal stability of $Pb(pta)_2$ in the presence of oxygen is much lower than in vacuo (Table 1). Temperature dependences of ion peak intensities for the major products of the complex decomposition in the presence of oxygen are shown in Fig. 7. Similarly to other β-diketonate complexes, the amount of CO_2 in the products of decomposition is much higher in the presence of oxygen than in vacuo. The decrease of $[O_2]^+$ peak intensity in the mass spectra takes place nearly at the same time as the decrease of metal-containing peak intensity and the increase of $[CO_2]^+$ occurs.

4. Discussion

On the basis of the analysis of gaseous decomposition products of $Cu(pta)_2$ and $Pb(pta)_2$, the schemes of heterogeneous thermal decomposition of these complexes are proposed on the assumption of isolated molecules $Cu(pta)_2$. Two routes of $Cu(pta)_2$ thermal decomposition are possible:

$$Cu(pta)_2 \xrightarrow{T > 350^\circ C} \{Cu, C\}_{solid} + \{Hpta, CF_3^{\cdot}, C_4H_9^{\cdot}, CHCO^{\cdot}, CO\}_{gaseous}$$

$$Cu(pta)_2 \xrightarrow{T > 400^\circ C} \{Cu, C\}_{solid} + \{CO, HF, H_2O\}_{gaseous}$$

The first route is decomposition with the formation of molecular products (pivaloyltrifluoracetone Hpta, CO) and radicals one (C_4H_9, CF_3). The second route of thermal decomposition is realized at higher temperatures and leads to the formation of simple gaseous products including carbon monoxide, HF and water.

A proposed scheme for $Pb(pta)_2$ thermal decomposition in vacuo is:

$$Pb(pta)_2 \overset{T>350°C}{\rightarrow} \{Pb, C\}_{solid} + \{Hpta, CF_3, C_4H_9, CHCO, CO\}_{gaseous}$$

It is assumed that in the first stage of decomposition an Hpta molecule is abstracted from the complex, and then subsequent abstraction of fragments from the residue occurs with the release of lead and carbon into the solid phase.

The comparison of complex decomposition products in vacuo and in the presence of hydrogen and oxygen indicates that the presence of H_2 and O_2 does not influence the mechanism of decomposition. However, in the presence of oxygen, two processes occur simultaneously: $Pb(pta)_2$ and $Cu(pta)_2$ thermal decomposition and the oxidation of ligand in the complex and of carbon. Oxygen reacts with $Pb(pta)_2$ and $Cu(pta)_2$ at the surface oxidizing only the organic part of complex. This process is accompanied by the release (into the solid phase) of metal, not oxide as may be expected. The formation of Pb during thermal decomposition of $Pb(pta)_2$ in vacuo and in the presence of oxygen has been confirmed by means of X-ray diffraction studies of the composition of films formed during thermal decomposition of the complex [13].

5. Conclusion

This study has determined the major gas-phase products formed during thermolysis of the complexes under investigation. Composition of gaseous products of copper(II) and lead(II) complexes with identical β-diketonates is similar. Hence, it can be assumed that thermolysis of these complexes proceeds via the same mechanism. Comparison of thermal behaviour of $Cu(pta)_2$ with that of copper β-diketonates studied earlier has shown that, whereas pivaloylfluoracetonate contains a trifluoromethyl group, its thermal behaviour resembles that of copper dipivaloylmethanate $Cu(C(CH_3)_3COCHCOC(CH_3)_3)_2$. In particular, thermal decomposition of this complex is accompanied by the evolution of free ligand into the gas phase, which has not been observed for other fluorinated β-diketonates of metals.

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