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Investigation of the thermal decomposition of bis(acetylacetonato)copper(II) vapour by a mass spectrometric method

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Abstract

The thermal destruction processes of bis(acetylacetonato)copper(II) (2,4-pentanedionato-copper(II), $Cu(aa)_2$) vapour and acetylacetone (2,4-pentanedione, Haa) were investigated using the high-temperature source of a molecular beam with mass spectrometric recording of the gas-phase composition. From the temperature dependence of the ion currents, the thermal stability of the ligand and complex was assessed and schemes of their thermal destruction in vacuo, hydrogen, and oxygen are suggested. The kinetic parameters of these processes are calculated.

Keywords: Bis(acetylacetonato)copper(II); Decomposition; Kinetics; MS; Pyrolysis

1. Introduction

Metal complexes of β-diketones (1,3-diones) are extensively applied as precursors for chemical vapour deposition (CVD) of metal and oxide films and coatings. These compounds are also used for obtaining phases with catalytic activity on a hard matrix, etc. [1]. A knowledge of the thermal destruction processes of the precursors (thermal stability, composition of thermolysis products, the influence of different additives) is necessary for choosing the CVD conditions and controlling parameters.

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The thermal decomposition processes of metal β-diketonates in the gas phase have rarely been investigated. Information on the thermal stability and thermolysis mechanism of some β-diketonates obtained from the literature was mainly determined from the analysis of the products of the decomposition of these complexes in condensed phase or vapour phase at a pressure above 100 Pa [2,3]. Under such conditions, secondary reactions between the gaseous products and with the initial compound in the condensed phase are highly probable. Owing to this, conclusions based on qualitative analysis of reaction products carried out under similar conditions concerning the mechanism of the thermal decomposition of complexes may be incorrect for vapours. Therefore, to study the thermolysis of metal β-diketonate vapours we used a mass spectrometric method, recording the gas-phase composition immediately on output from the reaction zone to obtain information about the primary products of reaction. Previously we have carried out similar investigations on vapour of the copper(II) complex with dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione) which are frequently used for production of HTSC films [4]. The complex of copper(II) with acetylacetone, which is the simplest β-diketone, is suitable for investigation because it is sufficiently volatile and can form either a metal or an oxide in the solid phase, depending on thermolysis conditions [5]. In addition, it is of interest to compare the thermal behaviour of acetylacetonate and dipivaloylmethanate complexes.

2. Experimental

2.1. Apparatus

To obtain data on the thermal decomposition of the ligand and complex vapour in vacuo and in different gas environments, we used the system based on the MSKh-6 (USSR) time-of-flight mass spectrometer (mass numbers up to 3000, resolution of 350 on a 50% level of peak height) with the special inlet system. The automatic system for accumulation and primary processing of data provided information about 20 different ion peaks of a mass spectrum and also about current values of temperature and pressure. When necessary, the full mass spectrum was recorded. The apparatus used is described in detail in Ref. [4].

2.2. Procedure

An ampule containing a sample was placed in the evaporator, which was evacuated and heated to 150°C for $Cu(aa)_2$; for the ligand, it was at room temperature. The saturated vapour pressure of $Cu(aa)_2$ at the temperature of the evaporator was 0.4 mbar [6]. Sample vapour was delivered via the opened valve through the heated pipeline to the thermal reactor, where decomposition took place. The vapour of the studied compound was mixed with a reagent gas before the inlet to the reactor. The reactor was heated linearly from 150 to 600°C for the complex and from 160 to 700°C for the ligand. The rate of heating was 2-3 K

min^{-1}. The working pressure in the vacuo chamber of the mass spectrometer was not higher than 9.3 mPa.

The temperature dependence of the intensity of the ion peaks of the complex, and the main products of its thermolysis in vacuo, hydrogen and oxygen, were used to study the thermal decomposition. Also analogous dependences were obtained for the free ligand and the products of its thermal decomposition. The experiments were carried out with ascending and descending temperature courses. Before investigations, in order to prepare the reactor surface, $Cu(aa)_2$ vapour was passed through the thermal reactor heated to high temperature. This was necessary to obtain reproducible results.

In addition, the dependence of the ion peak intensity of the products of $Cu(aa)_2$ thermal decomposition at 500°C was determined from the quantities of oxygen evolved.

3. Results and discussion

3.1. *Mass spectra of bis(acetylacetonato)copper(II) and acetylacetone*

The mass spectrum of bis(acetylacetonato)copper(II) is presented in Table 1. It is in good agreement with published data [7]. The peak with the maximum mass-to-charge ratio (m/z) corresponds to the molecular ion $[Cu(C_5H_7O_2)_2]^+$, indicating monomeric composition of the complex vapour.

The fragmentation process of the molecular ion under electron impact follows several paths. The first pathway results in $[Cu(C_5H_7O_2)]^+$ with further cleavage to $[CuCH_3COCHCO]^+$, $[CuOCCH_2]^+$ and $[Cu]^+$. The stepwise elimination of methyl groups resulting in ion peaks of 246 and 231 m/z is another pathway. The ion peak of 163 m/z appears to be connected with the migration of a hydrogen atom in the molecular ion and with the cleavage of one of the ligands. This process is the third pathway. The fragmentation of $[Cu(aa)_2]^+$ under electron impact is described in more detail in Refs. [7,8].

The abundance of the molecular ion peak of the ligand $[Haa]^+$ in the mass spectrum of $Cu(aa)_2$ has attracted attention. The mass spectrum of the complex in the range of light mass particles is very similar to that of the ligand (Table 1). Such a mass spectrum is also typical for the complex of copper with dipivaloylmethane; however, a similar agreement for other metal complexes with these ligands is not observed.

In the initial (without decomposition) mass spectrum of the ligand recorded at the temperature of the ionization chamber, 150°C (Table 1), together with a moderately intense (36%) molecular ion peak $[C_5H_8O_2]^+$, ion peaks $[CH_3COCH_2CO]^+$ (m/z 85) and $[CH_3CO]^+$ (m/z 43) with relative intensities (I_{rel}) of 61% and 100%, respectively, and fragments with relative intensities no higher than 4% (with the exception of the ion peak with m/z 28, $I_{rel} = 11.5\%$), are presented. Some aspects of acetylacetone behaviour under electron impact are given in Ref. [9].

Table 1
Mass spectra of bis(acetylacetonato)copper(II) and acetylacetone

Ion [a]	*m/z*	Relative intensity in %		
		$Cu(aa)_2$ 70 eV, 177°C	$Cu(aa)_2$ [4] 80 eV, 200°C	Haa 70 eV [b], 150°C [c]
$[CuC_{10}H_{14}O_4]^+$	261	36	24	–
$[CuC_9H_{11}O_4]^+$	246	18	14	–
$[CuC_8H_8O_4]^+$	231	15	11	–
$[CuC_5H_8O_2]^+$	163	12	–	–
$[CuC_5H_7O_2]^+$	162	19	14	–
$[CuC_4H_4O_2]^+$	147	23	20	
$[CuC_2H_2O]^+$	105	10	9	–
$[Cu]^+$	63	8	–	–
$[C_5H_8O_2]^+$	100	34	41	36
$[C_4H_5O_2]^+$	85	48	51	61
$[C_4H_8O]^+$	72	8	6	4
$[C_3H_6O]^+$	58	5	4	2
$[C_2H_3O]^+$	43	100	100	100
$[CO_2]^+$	44	9	–	4
$[CO]^+$	28	14	2	11.5
$[H_2O]^+$	18	6	–	4
$[CH_3]^+$	15	8	–	4

[a] Here copper-containing ions are presented as the more naturally occurring isotope ^{63}Cu. [b] Ionization voltage. [c] Thermal reactor inlet temperature.

3.2. *Thermal decomposition of acetylacetone in vacuo and various gas environments*

For reliable interpretation of the thermal behaviour of $Cu(aa)_2$ vapour, mass spectra of acetylacetone at various temperatures and the temperature dependences of the ion currents of the ligand and its thermal decomposition products in vacuo, oxygen and hydrogen were obtained.

In the mass spectra of the ligand recorded in vacuo at higher temperatures than that for the initial mass spectrum, the intensities of the molecular ion peak and its fragments decrease. A peak with *m/z* 28 corresponding to $[CO]^+$ is the most intense, i.e. carbon(II) oxide is a main product of acetylacetone thermal decomposition.

The temperature dependences of the ion peak intensities of acetylacetone and the products of its thermal decomposition in vacuo are shown in Fig. 1. The thermal decomposition in hydrogen is very similar. The temperature at which a sharp reduction in the molecular ion peak intensity was observed (the so-called decomposition threshold temperature T_d) was accepted as the temperature of the onset of thermolysis of the compound. We used this temperature for a qualitative evaluation of the thermal stability of the compound. The threshold temperature of Haa decomposition in vacuo is 565 ± 10°C. In hydrogen, this temperature is practically

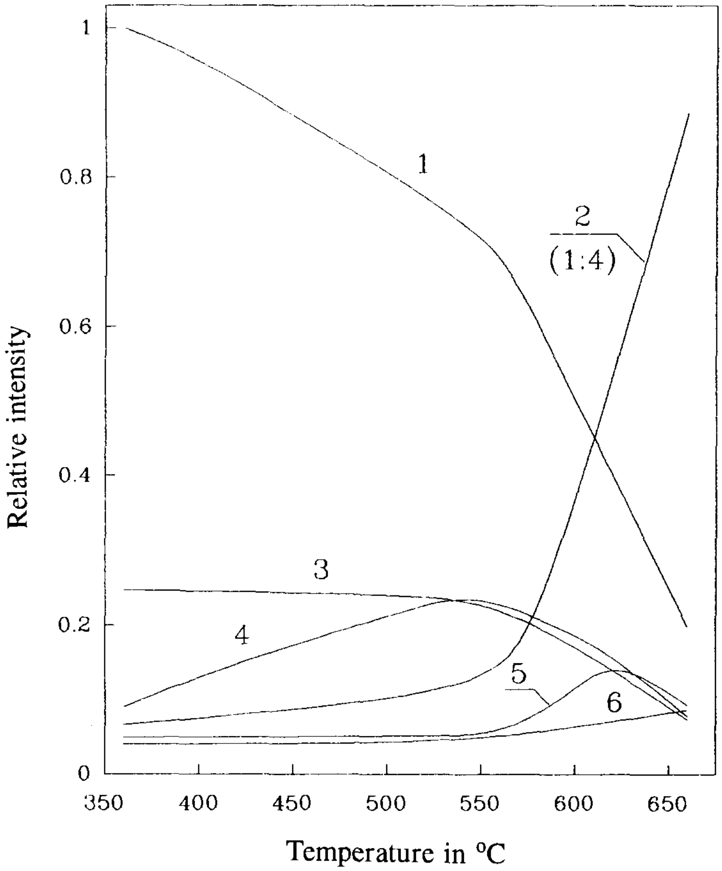
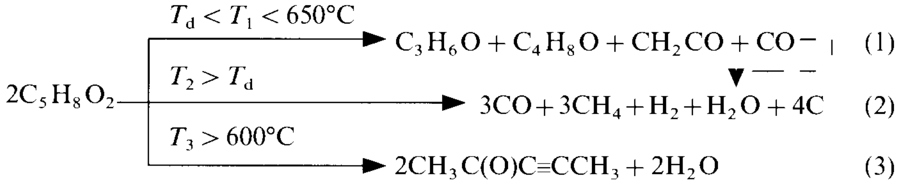


Fig. 1. Temperature dependences of ion peak intensities of acetylacetone and the products of its thermolysis in vacuo: 1, $[Haa]^+$; 2, $[CO]^+$; 3, $[CH_3COC_2H_5]^+$; 4, $[CH_3COCH_3]^+$; 5, $[H_2O]^+$; 6, $[CH_4]^+$.

unchanged. The mass spectra of the products can be superimposed on the mass spectrum of the initial substance recorded under thermal decomposition conditions. With temperature increase, the intensities of the m/z 58 and 72 ion peaks (corresponding to acetone and ethylmethylketone, respectively) and the molecular ion peak become disproportionate suggesting that these ions are not only the result of ligand fragmentation under electron impact, but also belong to the products of its thermal decomposition. The temperature dependences of the acetone and ethylmethylketone ion peaks pass through a maximum; therefore, these compounds are thought to be intermediates. Such a conclusion agrees with the principle of minimum rearrangement of atoms in a molecule on formation of intermediate products. At higher temperatures, the thermolysis products are mainly carbon(II) oxide, methane and water. From the analysis of the full mass spectra recorded at various temperatures and the temperature dependences, we suggest Eqs. (1)–(3) for the description of the thermal decomposition of acetylacetone in vacuo and hydrogen.



$$2C_5H_8O_2 \xrightarrow{T_d < T_1 < 650^\circ C} C_3H_6O + C_4H_8O + CH_2CO + CO \quad (1)$$

$$2C_5H_8O_2 \xrightarrow{T_2 > T_d} 3CO + 3CH_4 + H_2 + H_2O + 4C \quad (2)$$

$$2C_5H_8O_2 \xrightarrow{T_3 > 600^\circ C} 2CH_3C(O)C{\equiv}CCH_3 + 2H_2O \quad (3)$$

According to this scheme, the thermolysis of Haa in vacuo and hydrogen proceeds in three directions depending on temperature. It should be noted that Eq. (1) can be an individual reaction as well as an intermediate stage in Eq. (2). Taking into account the fact that the curve of the temperature dependence of the $[H_2O]^+$ intensity passes through a maximum in the range 610–640°C, the existence of a secondary reaction (interaction between the products themselves) can be assumed

$$H_2O + C \rightarrow CO + H_2$$

At temperatures above 600°C, another direction of the Haa thermal decomposition, a dehydration process, takes place. This is evident from the appearance of an ion peak with *m/z* 82 ($CH_3C(O)C{\equiv}CCH_3$) and its fragment with *m/z* 39 in the mass spectrum.

The relative quantities of the gaseous products of reaction were estimated from the intensity of the appropriate ion peaks of the mass spectrum and from values of the cross sections of molecular ionization given in Ref. [10].

The mass spectrum of the ligand heated in oxygen up to 560°C contains only ion peaks of the products of thermal oxidative destruction (carbon oxides, water and methane). The ratio of the main products of the thermal decomposition, CO_2, CO and H_2O, is 1 : 2.5 : 3.7, respectively. The temperature dependences of the intensity of $[Haa]^+$ and the ion peak of the products of acetylacetone thermal decomposition in oxygen are shown in Fig. 2.

It should be noted that in oxygen the thermal stability of the ligand is considerably lowered. The threshold temperature of Haa thermolysis is 300 ± 10°C in this case.

The data presented in this work complement a previous investigation on the pyrolysis of acetylacetone [11] in which the products of the process were determined. The presence of small amounts (about 8%) of acetic acid in pyrolysis products reported in Ref. [11] were not recorded by us. We believe that this product resulted from the secondary reactions which occur at favourable experimental conditions.

3.3. Thermal decomposition of bis(acetylacetonato)copper(II) vapour in vacuo and in hydrogen

The temperature dependences of the intensity of the main ion peaks of the mass spectrum, describing the composition of the gas phase on thermal decomposition of bis(acetylacetonato)copper(II) in vacuo, are presented in Fig. 3(a).

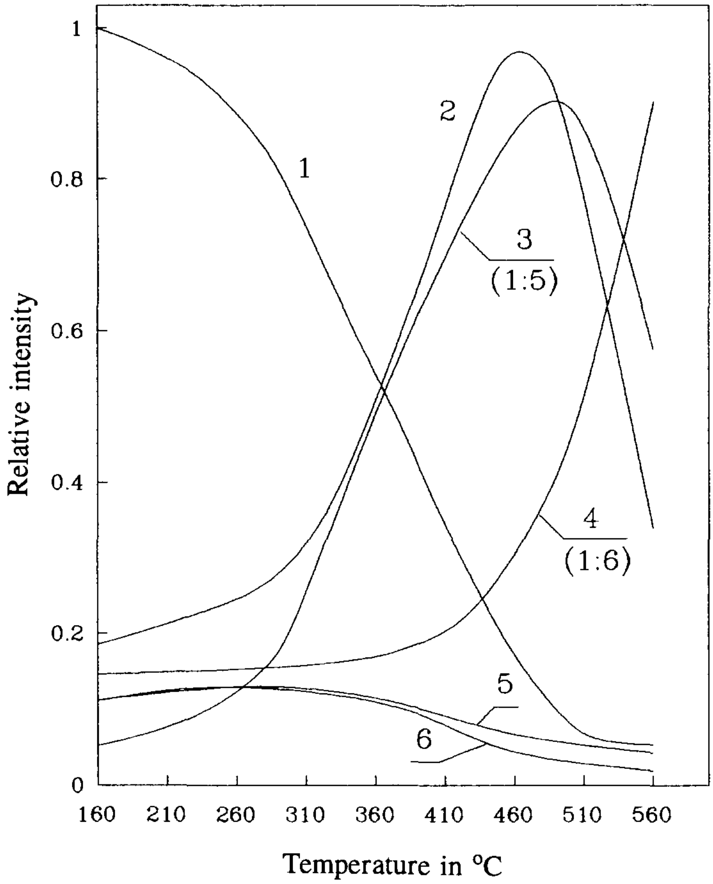
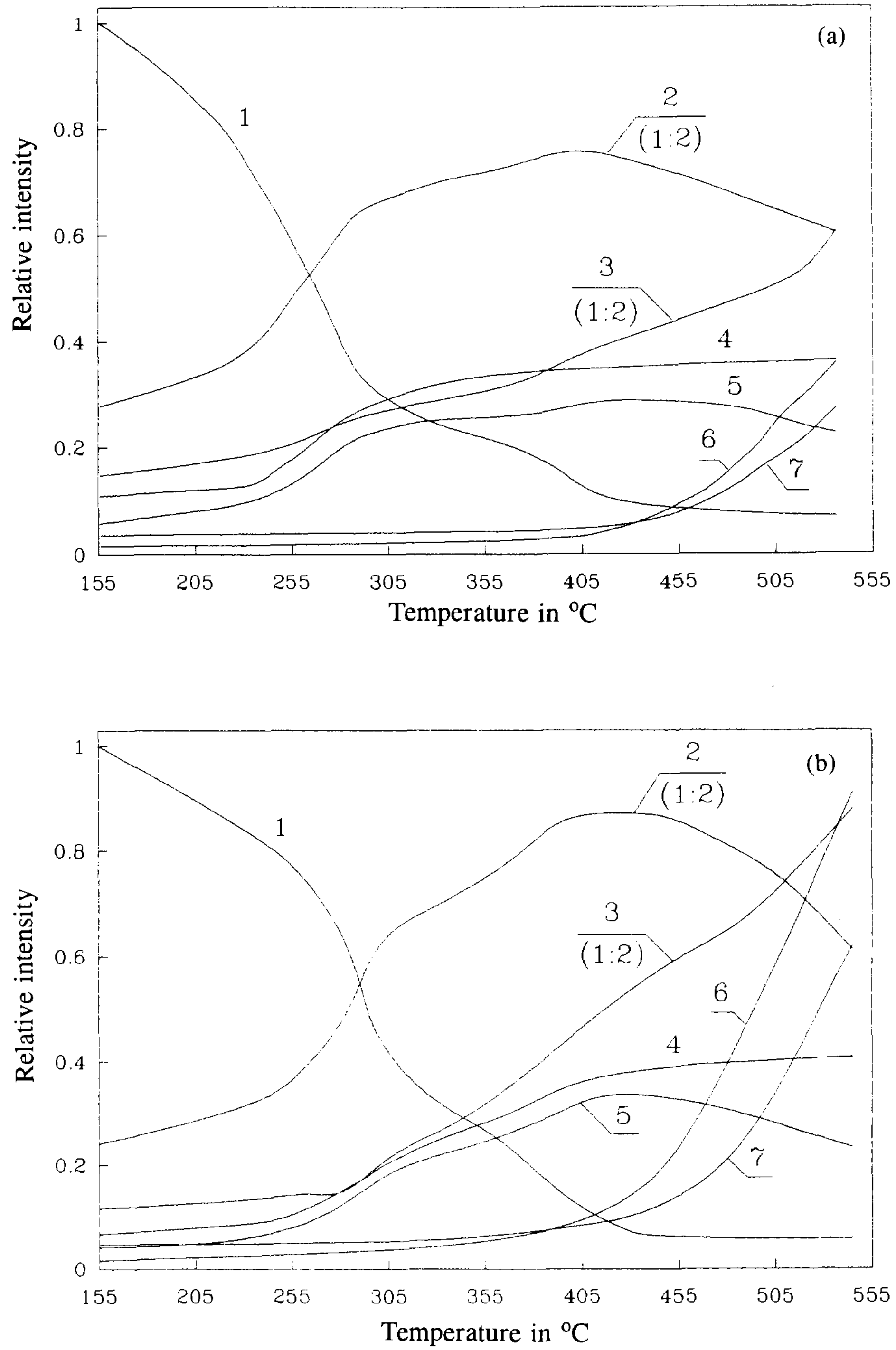


Fig. 2. Temperature dependences of ion peak intensities of acetylacetone and the products of its thermolysis in oxygen: 1, $[Haa]^+$; 2, $[H_2O]^+$; 3, $[CO_2]^+$; 4, $[CO]^+$; 5, $[CH_3COCH_3]^+$; 6, $[CH_3COC_2H_5]^+$.

Decomposition of the complex in vacuo begins at 230 ± 10°C. The thermal decomposition of the complex proceeds with liberation of the free ligand in the gas phase. In our opinion, the elimination of the Haa molecule proceeds by the migration of a hydrogen atom from one chelate ring to another. It is reasonable to suppose that this reaction takes place on the surface with opening of a chelate ring. The presence of the thermal decomposition products of the dehydrogenated ligand (acetone, ethylmethylketone, ketene) is evidence in favour of an intramolecular reaction. Such a complex decomposition and free ligand formation is confirmed by the identical change in intensity of all the metal-containing peaks with increasing temperature. This excludes the thermal dissociation of the complex according to [12] $Cu(aa)_2 \rightarrow Cu(aa)^{\bullet} + aa^{\bullet}$. The quantity of carbon oxides and water in the gas phase increase with increasing temperature. This clearly demonstrates a thorough destruction of the complex.


(a)
Relative intensity
1
0.8
0.6
0.4
0.2
0
155
205
255
305
355
405
455
505
555
Temperature in °C
1
2
(1:2)
3
(1:2)
4
5
6
7
(b)
Relative intensity
1
0.8
0.6
0.4
0.2
0
155
205
255
305
355
405
455
505
555
Temperature in °C
1
2
(1:2)
3
(1:2)
6
4
5
7

At 420–440°C, the intensity of the molecular ion peak and other metal-containing peaks become close to zero. This suggests that the compound was completely decomposed. The amount of ligand is maximum at this temperature.

It should be noted that the peak with m/z 84 ($CH_3C(O)CH{=}CO$) and its fragment with m/z 69 arise in the mass spectrum at high temperatures (about 400°C). Also an increase in the quantity of methane occurs above this temperature. The absence of such particles in the mass spectrum of the free ligand heated to these temperatures supports their formation by destruction of the complex.

Figs. 3(a) and (b) show that gas-phase composition is slightly changed in the range 300–380°C. It can be assumed that the thermolysis which is an aggregation of dehydrogenated copper-containing fragments occurs with formation of polychelates. Formation of the polymeric product was described in Ref. [13]. Further increase in temperature results in the destruction of the polychelates and formation of other condensed phases. The liberation of new gaseous products takes place simultaneously in accordance with Eq. (6) of the $Cu(aa)_2$ thermal decomposition scheme. The composition of the gas phase is the same on heating the complex in hydrogen and in vacuo (Fig. 3(b)). The threshold temperature is 280 ± 10°C. Thus, it is possible to assume the scheme shown in Eqs. (4)–(6) for bis(acetylacetonato)copper(II) thermal decomposition

$$\mathrm{Cu(aa)_2} \xrightarrow{T_1 > T_d} \text{solid phase} + \begin{bmatrix}\text{Haa, acetone,}\\ \text{ethylmethylketone,}\\ \text{ketene, CO}\end{bmatrix} \tag{4}$$

$$\mathrm{Cu(aa)_2} \xrightarrow{T_2 > T_d} \text{solid phase} + \begin{bmatrix}\text{carbon(II) oxide,}\\ \text{water}\end{bmatrix} \tag{5}$$

$$\mathrm{Cu(aa)_2} \xrightarrow{T_3 \geq 400^\circ\mathrm{C}} \text{solid phase} + \begin{bmatrix}\mathrm{CH_3C(O)CH{=}CO,}\\ \text{methane}\end{bmatrix} \tag{6}$$

An earlier investigation of the thermal stability of bis(acetylacetonato)copper(II) vapour by a mass spectrometric method was reported in Ref. [14]. The authors determined the temperature of the start and total decomposition of $Cu(aa)_2$. The increase in the ratio of the $[Cu(aa)]^+$ to $[Cu(aa)_2]^+$ ion currents with temperature increase was interpreted as evidence of a thermal decomposition. In our view, this can be caused by the fragmentation of thermally excited molecules of $Cu(aa)_2$ under electron impact (as we noted for copper(II) dipivaloylmethanate). This can be checked by cooling heated vapour from an outlet from the thermal reactor to a temperature close to that of the evaporator. Retention of the dependence of the

Fig. 3. (a) Temperature dependences of ion peak intensities of bis(acetylacetonato)copper(II) and the products of its thermal decomposition in vacuo: 1, $[Cu(aa)_2]^+$; 2, $[Haa{-}CH_3]^+$; 3, $[CO]^+$; 4, $[CH_2CO]^+$; 5, $[CH_3COCH_3]^+$; 6, $[CH_3C(O)CH{=}CO]^+$; 7, $[CH_4]^+$.
(b) Temperature dependences of ion peak intensities of bis(acetylacetonato)copper(II) and the products of its thermal decomposition in hydrogen: 1, $[Cu(aa)_2]^+$; 2, $[Haa{-}CH_3]^+$; 3, $[CO]^+$; 4, $[CH_2CO]^+$; 5, $[CH_3COCH_3]^+$; 6, $[CH_3C(O)CH{=}CO]^+$; 7, $[CH_4]^+$.

ratio of $[Cu(aa)]^+$ to $[Cu(aa)_2]^+$ ion currents at the reactor temperature is evidence that this ratio is related to thermal decomposition [4].

3.4. Thermal decomposition of bis(acetylacetonato)copper(II) vapour in oxygen

In an oxygen environment, the threshold temperature of the complex decomposition is 235 ± 10°C. As can be seen in Fig. 4, the qualitative composition of the gas phase is not notably changed on thermal decomposition of the complex in oxygen. Therefore, it is possible to assume that the process of $Cu(aa)_2$ vapour decomposition proceeds in the same directions as in vacuo. However, above 300°C destruction of the ligand also occurs. An abundance of CO_2 and a significant increase in the amount of CO and H_2O in the products of $Cu(aa)_2$ decomposition in oxygen, in comparison with in vacuo, is connected with this. Such a conclusion agrees with the

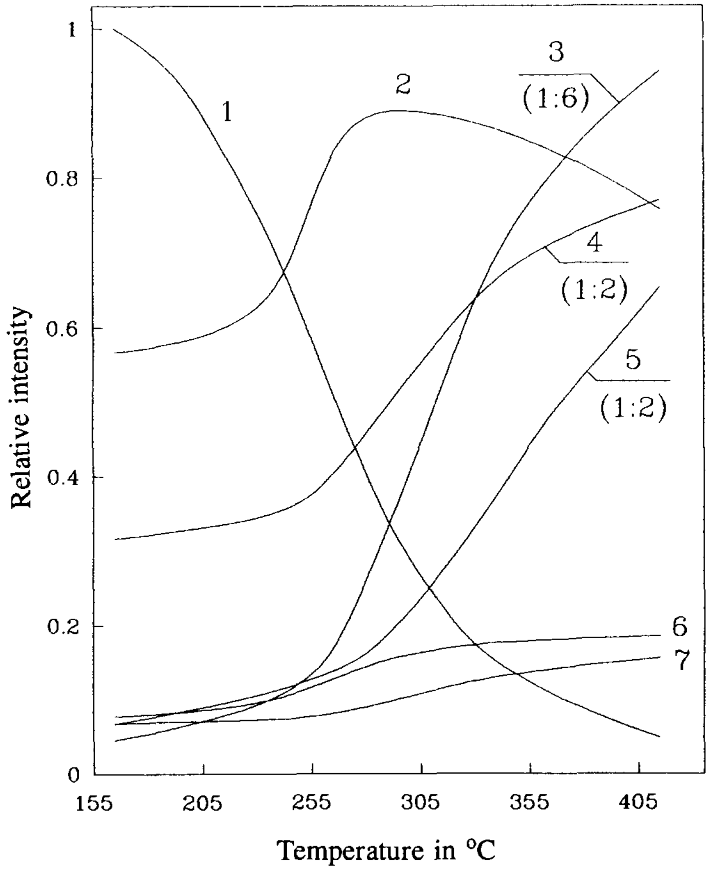


Fig. 4. Temperature dependences of ion peak intensities of bis(acetylacetonato)copper(II) and the products of its thermal decomposition in oxygen: 1, $[Cu(aa)_2]^+$; 2, $[Haa-CH_3]^+$; 3, $[CO_2]^+$; 4, $[CO]^+$; 5, $[H_2O]^+$; 6, $[CH_3COCH_3]^+$; 7, $[CH_4]^+$.

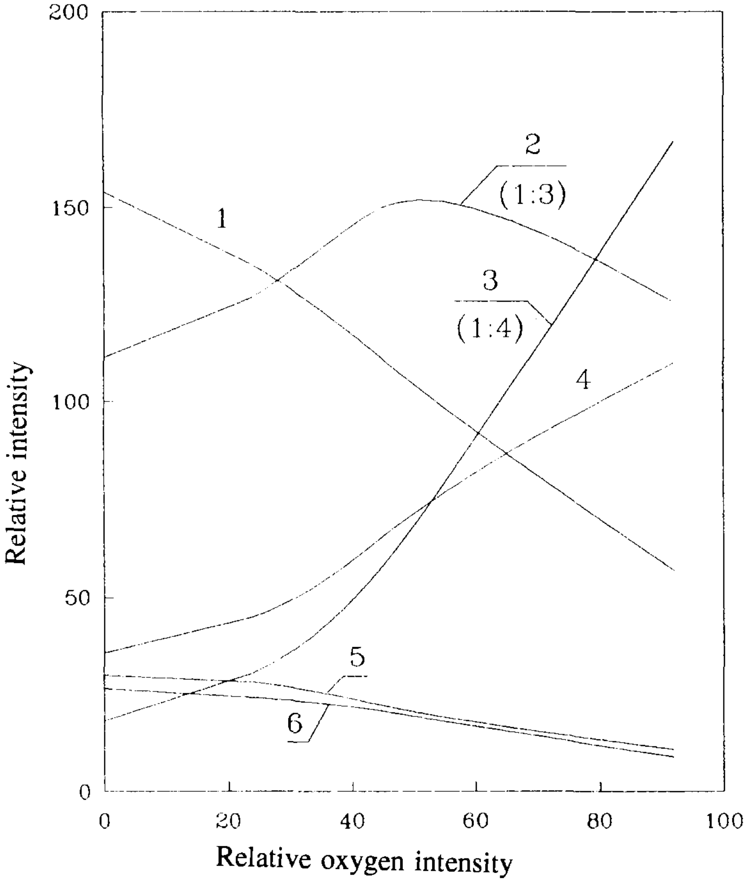


Fig. 5. Dependences of ion peak intensities of bis(acetylacetonato)copper(II) thermolysis products on the quantity of oxygen (temperature, 500°C): 1, $[Haa]^+$; 2, $[CO]^+$; 3, $[CO_2]^+$; 4, $[H_2O]^+$; 5, $[CH_3C(O)CH{=}CO]^+$; 6, $[CH_3COCH_3]^+$.

results of the study of the free ligand decomposition in oxygen. It is also supported by the behaviour of the oxygen peak intensity, which starts to decrease significantly at temperatures above the Haa decomposition threshold temperature simultaneously with the reduction of the ligand quantity. A similar behaviour on heating in oxygen was observed by us in the case of the complex of copper with dipivaloylmethane [4].

The relative quantity of oxygen does not change the qualitative composition of the gas phase in practice, but influences the reaction rate, which increases with an increase in oxygen in the reaction zone. Fig. 5 shows the dependence of the molecular ion peak intensities of the thermolysis products on the amount of oxygen. It is clear that an increase in oxygen causes an increase in the deeper oxidation products.

3.5. Kinetic parameters of thermal decomposition

The rate constant of a first-order reaction for the initial compound was calculated from the temperature dependences of the molecular ion peak intensity using the empirical relation given below which was developed from the balance equation of the initial compound particles in the thermal reactor (molecular flow and no reverse reaction)

$$K = \{(A_t + A_e)(T/M)^{1/2}[(I_{0i}/I_i)(T_0/T)^{1/2} - 1]\}/V$$

where A_t and A_e are constants related to the gas flow conductivity ($F_t = A_t(T/M)^{1/2}$) of the pipelines connecting the evaporator with the reactor and the effusion outlet of reactor, respectively (determined from the geometrical sizes), I_{0i} the intensity of the initial compound ion peak measured at any temperature T_0 before the threshold of thermal stability, I_i the current value of the ion peak intensity

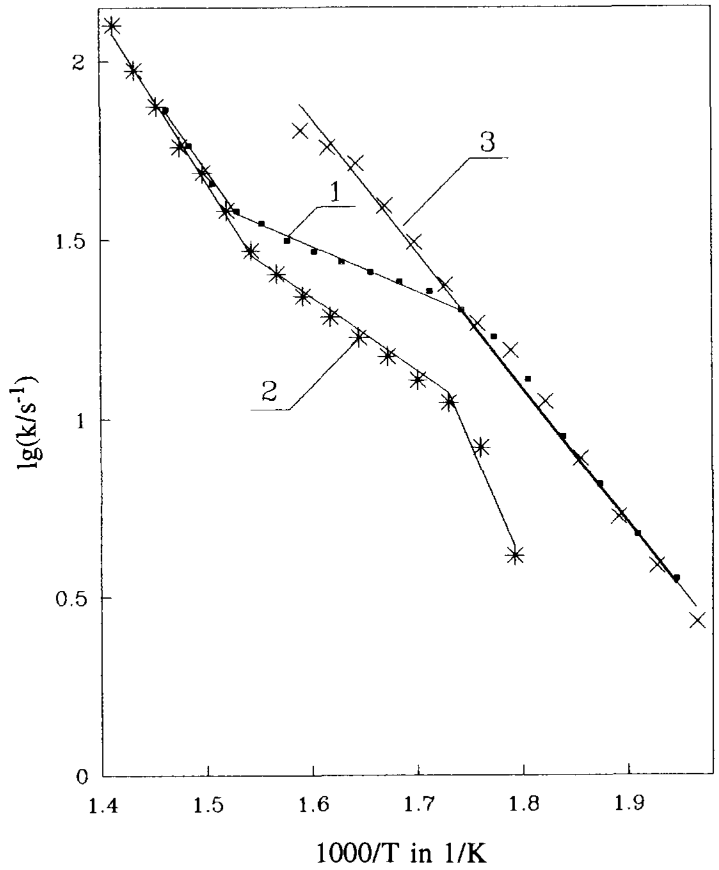


Fig. 6. Dependence of the logarithm of the rate constant on temperature for $Cu(aa)_2$ thermal decomposition in vacuo (1), hydrogen (2), and oxygen (3).

Table 2
Kinetic parameters of $Cu(aa)_2$ thermal decomposition

Gas environment	Temperature range in °C	E_a in (kJ mol^{-1})	K_0 in s^{-1}
Vacuum	240–300	73.8 ± 1.9	1.11×10^8
	300–380	23.6 ± 0.8	2.82×10^3
	380–410	82.2 ± 2.1	1.38×10^8
Hydrogen	285–305	133.0 ± 12.4	1.25×10^{13}
	305–375	42.6 ± 0.9	7.79×10^4
	375–435	89.9 ± 2.8	5.14×10^8
Oxygen	235–355	72.0 ± 2.2	7.22×10^7

measured at temperature T, V the volume of the reactor, and M the molecular mass of the initial compound.

The kinetic parameters in the Arrhenius equation were calculated from the temperature dependence of the reaction rate constant. These parameters correspond to the overall process of the thermal decomposition of an initial compound.

The close effective values of activation energy (E_a) and pre-exponential factor (K_0) for the thermal decomposition of acetylacetone in vacuo and hydrogen ($E_a = (92.7 \pm 6.3)$ and (87.6 ± 3.4) kJ mol^{-1}, $K_0 = 4.86 \times 10^6$ and 2.40×10^6 s^{-1}, respectively), as well as the data on the composition of the gaseous products, confirm that both processes proceed with an identical mechanism. Values of the kinetic parameters of the acetylacetone thermal decomposition in oxygen are: $E_a = (87.8 \pm 1.9)$ kJ mol^{-1}; $K_0 = 1.42 \times 10^8$ s^{-1}. The temperature dependences of the $Cu(aa)_2$ thermal decomposition rate constants are displayed in Fig. 6. The temperature curves of $[Cu(aa)_2]^+$ intensity obtained on thermal decomposition in vacuo and in hydrogen have three distinct parts (Fig. 3(a) and (b)). The temperature dependences of log K also consist of three sections. Each is characterized by its own kinetic parameter values determined from the Arrhenius equation. The effective values of these parameters are listed in Table 2. These stages are a result of the rate of thermal decomposition in these temperature ranges being controlled by various reactions proceeding in parallel (see scheme for $Cu(aa)_2$ thermal decomposition). Low values of the kinetic parameters in the range 300–380°C are probably owing to the formation of copper polychelates. This phenomenon is not observed on thermal decomposition of $Cu(aa)_2$ in oxygen.

4. Conclusions

In the thermal decomposition of the complex and ligand in vacuo and in hydrogen, the composition of the gaseous products of reaction is the same and the process can be described by the same schemes. However, the thermal stability of bis(acetylacetonato)copper(II) in hydrogen is increased (by approximately 50°C).

Oxygen has a significant effect on the thermal decomposition of the ligand, decreasing its thermal stability by 265°C.

A comparison of the data obtained for thermolysis of the complex with those for $Cu(dpm)_2$ vapour shows that the temperature of decomposition onset for the acetylacetonate complex is lower. In contrast with $Cu(dpm)_2$, whose thermal stability decreases on heating in oxygen, the thermal stability of $Cu(aa)_2$ is practically unchanged on heating in oxygen from the results in vacuo.

The thermal decomposition of the ligand and complex proceeds in several stages according to the schemes given and kinetic parameters deduced. It is believed that the nature of the thermal reactor surface affects the thermolysis, i.e. thermal decomposition is a complex heterogeneous process. The suggested scheme of bis(acetylacetonato)copper(II) decomposition still requires some elucidation; the fact that the products are in the solid phase will make analysis more straightforward.

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