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MASS SPECTROMETRIC STUDY OF THERMAL STABILITY OF COPPER(II) BIS(DIPIVALOYLMETHANATE) VAPOUR

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The processes of thermal destruction of copper(II) bis(dipivaloylmethanate) (Cu(dpm)$_2$) in the temperature range 150°–550°C were studied by using a two-temperature variant of a double chamber Knudsen cell, with mass spectrometric recording of the gas-phase composition. The temperature range of stability of the vapour of the complex in vacuum was determined, as were those of its mixtures with oxygen in different proportions. The temperature dependence of the rate constant of the thermolysis of (Cu(dpm)$_2$) vapour was obtained. The thermal stability of Hdpm vapour and the influence of oxygen on the thermolysis of the ligand were studied.

Keywords: copper(II) bis(dipivaloylmethanate), kinetic parameters, mass spectrometry, superconducting films, thermal stability

Introduction

The increasing interest in β-diketonates of such metals as yttrium, barium, copper and others in mainly due to their application [1] in gas-phase thermolysis for the production of superconducting films and coatings. Metal complexes of dipivaloylmethanate (Hdpm) and heptafluoromethyloctanedionate (Hfod) are the most frequently used initial components [2, 3]. However, despite all the successes in the production of superconducting films from metal β-diketonates, questions concerning the thermal stability of these compounds in various states of aggregation remain practically uninvestigated. A study of the influence of oxygen on the thermolysis processes appears most important. At present, data are available on the volatility (the pressure of the saturated vapour of the majority of copper(II) β-diketonates [4], with contradictory results on the volatility of Y(dpm)$_3$ [5, 6]. However, there is no information on the pressure of the saturated vapour of other β-diketonate derivates of yttrium or of the complexes of barium. There may well be developed approaches and standard techniques for investigation of the thermal stability of volatile compounds in the condensed phase, but study of the gas-phase

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thermal stability and of gas-phase processes requires the development of new approaches. The known techniques for investigation of the gas-phase thermal stability of organometallic compounds, with mass spectrometric detection of the reaction products [7], provide information about the products largely formed in secondary processes. The aim of the present work is to study the processes of thermal destruction of Cu(dpm)$_2$ vapour alone or in mixtures with oxygen, and to determine the kinetic parameters.

Experimental

For study of the processes of thermal destruction of the copper complex and the ligand in the gas phase, we used the system based on the MSKh-6 (USSR) time-of-flight mass spectrometer, with a mass number range 1000–3000 M/Z and a mass resolution of 350 at 50% of the peak height. The accumulation and primary processing of the data were carried out under real-time conditions. The current temperature and pressure in the system, and also the intensity and integral intensity values for not more than 20 different ion peaks in the spectrum of the compound under study were also recorded. When necessary, the full mass spectrum was recorded.

The thermal stability of Cu(dpm)$_2$ and Hdpm under different conditions was studied by using the temperature dependence of the intensities of the ion peaks in

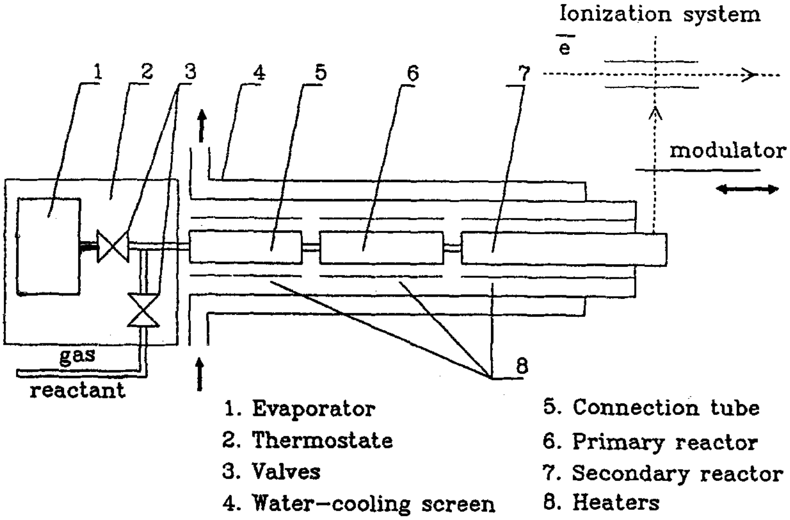

Fig. 1 Diagram of the system of injection of the vapour of compounds under study into the mass spectrometer

the mass spectrum of the vapour of the compound under study, and also the products of its thermolysis. For this purpose, the mass spectrometer had a special injection system.

A schematic diagram of the injection system for the vapour of the studied compound is shown in Fig. 1. It is similar to the two-temperature variant of the Knudsen effusion method with a double chamber.Parts 6 and 7 of the chamber can be heated independently. Such a construction allows performance of the reaction in either chamber 6 or chamber 7. During the usual experiments, thermolysis of the vapour takes place in chamber 7, and the detected flow of particles bears information about the processes occurring directly in the reaction zone. Application of chamber 6 as a reactor is necessary when the temperature variations give rise to only a quantitative change in the mass spectrum. During these experiments, vapour heated to the necessary temperature is cooled in chamber 7 to a temperature close to that of evaporation. If the observed variations in the mass spectrum are due to fragmentation of the excited molecules, then the excited states of the molecule are quenched as a result of collision with the cool wall, and the observed mass spectrum does not depend on the temperature of reactor 6. If this dependence is retained, the observed variations are due to the decomposition processes.

The compound under study was placed into evaporation chamber 1, the chamber was evacuated and heated to a certain temperature, and the evaporating sub-

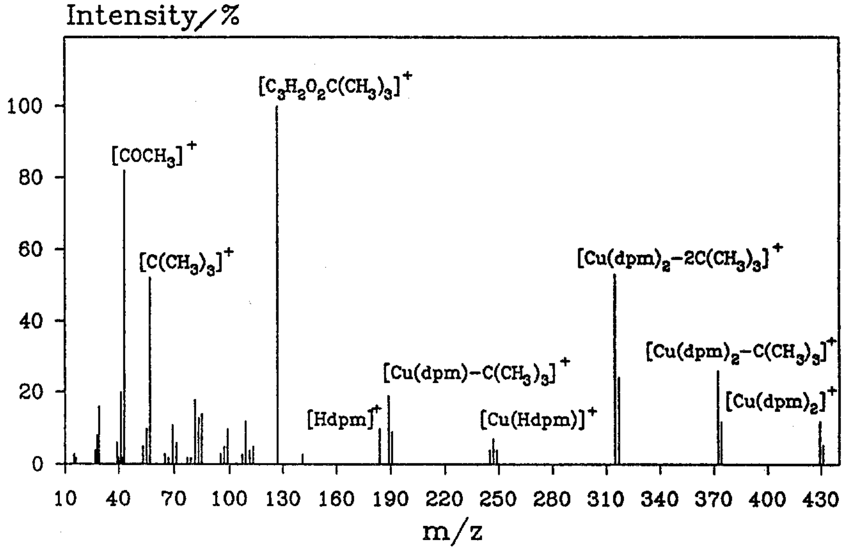

Fig. 2 Mass spectrum of copper(II) bis(dipivaloylmethanate)

stance was delivered through heated valve 3 to connecting pipeline 5, where it was mixed with reagent gas. Only after this did the vapour of the compound pass into the reaction zone. The outlet from the reaction zone was the effusion aperture, 0.3 mm in diameter. It was located relative to the ion source of the mass spectrometer in such a manner that the molecular flow of the substance passed directly into the ionization chamber of the instrument. At the effusion outlet, the molecular flow was modulated by a mobile shutter, which allowed separation of the useful signal from the background.

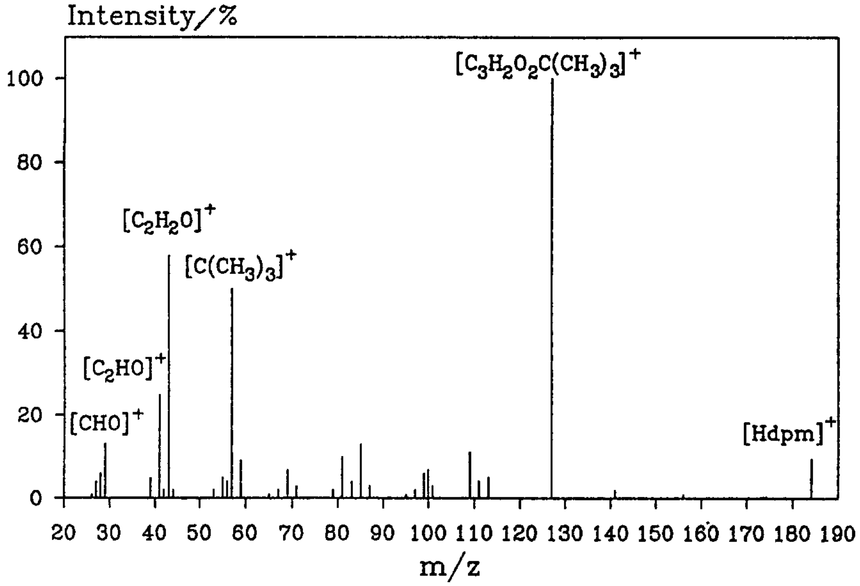

Fig. 3 Mass spectrum of Hdpm

To obtain the temperature dependence, the reactor was heated linearly at a rate of 2.5 deg/min, starting as a rule from a temperature 1020 deg higher than that of the evaporation chamber. The experiments were carried out under the conditions of the direct and reverse courses of temperature. The maximum possible temperatures of the evaporation chamber and the decomposition zone are 300° and 750°C, respectively. All parts of the injection system are made from stainless steel.

$Cu(dpm)_2$ was studied at 120°C in the evaporator zone; according to [4], this corresponds to a saturated vapour pressure of $4\cdot10^{-2}$ Torr. In the zone where the compounds studied underwent thermolysis, the temperature was varied in the range from 150° to 600°C. In the experiments involving the use of oxygen, its amount in the mixture was varied between limits of 3 to 12 times the amount of $Cu(dpm)_2$. The quantitative ratio of the components was calculated by using the intensities of the ion peaks in the mass spectrum, the theoretical ionization crosssections and the additivity law [8]. In all experiments, the working pressure in the analyzer was not greater than $5 \cdot 10^{-6}$ Torr, with a residual pressure at the level of $3 \cdot 10^{-8}$ Torr.

Results and discussion

Mass spectrum of Cu(dpm)$_2$

The mass spectrum of Cu(dpm)$_2$) is shown in Fig. 2. Its characteristic feature is the presence apart from the molecular ion $[Cu(dpm)_2]^+$, M/Z=429 for ^{63}Cu of fragments $[Cu(dpm)_2C(CH_3)_3]^+$ and $[Cu(dpm)_2\text{-}2C(CH_3)_3]^+$ (M/Z=372 and 315, respectively), resulting from the abstraction of one and two t-Bu groups from the complex molecule, and also of peaks corresponding to the ions $[Cu(Hdpm)]^+$,

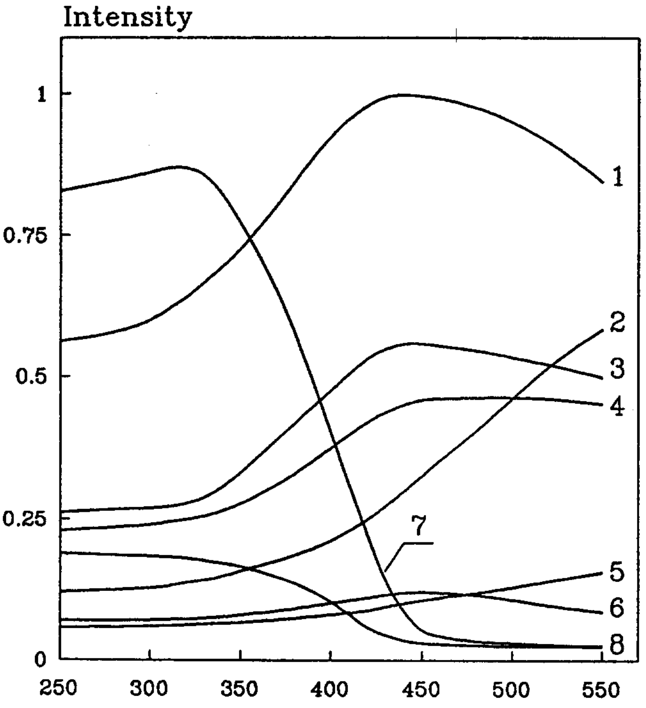

Fig. 4 Temperature dependence of intensities of ion peaks corresponding to the main products of thermal decomposition of copper(II) bis(dipivaloylmethanate) vapour: $[C_3H_2O_2C(CH_3)_3]^+$ (1), $[C_2HO]^+$ (2), $[C_2H_3O]^+$ (3), $[C(CH_3)_3]^+$ (4), $[CO]^+$ (5), $[Hdpm]^+$ (6), $[Cu(dpm)_2\text{–}2C(CH_3)_3]^+$ (7) and $[Cu(dpm)_2]^+$ (8)

$[Cu(dpm\text{-}H)]^+$ and $[Cu(dpmC(CH_3)_3)]^+$, with mass numbers M/Z=247, 245 and 189. The peak 315 M/Z has highest intensity. The mass spectrum of particles not containing metal is very similar to that of Hdpm (Fig. 3), with insignificant differences in the relative intensities of the peaks. We shall not go into the details of the fragmentation pathways of the molecules under study, since this is not the aim of the present article. It is merely noted that the vapour consists of monomeric $Cu(dpm)_2$ and the general character of the spectrum accords with the regularities of the behaviour of divalent metal chelates under electron impact [9].

Thermolysis of $Cu(dpm)_2$ vapour

Figure 4 shows the temperature dependence of the intensities of the ion peaks characterizing the gas-phase composition at the outlet from the reaction zone for $Cu(dpm)_2$ vapour. At temperatures above 330°±10°C, a decrease in intensity of the metal-containing ion peaks is observed (Fig. 4 shows only the $[Cu(dpm)_2]^+$ and $[Cu(dpm)_2\text{-}2C(CH_3)_3]^+$ peaks), and a simultaneous increase in intensity of the peaks characteristic of the Hdpm mass spectrum: $[Hdpm]^+$, $[C_3O_2H_2C(CH_3)_3]^+$, $[C_2H_3O]^+$ and $[C(CH_3)_3]^+$. The maximum in the temperature curve for $[Cu(dpm)_2\text{-}2C(CH_3)_3]^+$ is defined by the peculiarity of fragmentation of excited $Cu(dpm)_2$ molecules under electron impact during heating of the vapour in the studied temperature range.

With temperature rise in the reaction zone, there is a continuous decrease in concentration of the initial molecules, and the Hdpm concentration reaches its maximum in the temperature range 440°–450°C, with a subsequent decrease. At this temperature, the concentration of $Cu(dpm)_2$ is close to zero, which means practically complete decomposition of $Cu(dpm)_2$ molecules in the reactor. The maximum in the Hdpm curve may be connected with the decomposition of free β-diketone ligand at temperatures above 450°C. The monotonous increase in peak intensity for $[CO]^+$ and $[C_2HO]^+$ in Fig. 4 in the temperature range above 330°C allows the assumption that these peaks are related to the products of destruction of $Cu(dpm)_2$.

Kinetic parameters of thermolysis of $Cu(dpm)_2$ vapour

The kinetic parameters of $Cu(dpm)_2$ thermolysis can be calculated from the temperature dependence of the peak intensities of the metal-containing ions by using the equation for the variation of particle number in reaction volume at the given temperature, expressed in terms of ion current intensities [10]:

$$\frac{dJ^i}{dt} = W_f^i - W_c^i + \frac{G_o - G_p}{V}\left[\frac{(T_s \cdot T_o)^{1/2}}{T} \cdot J_o^i - J^i\right]$$

where W_f^i and W_c^i are the rates of formation and consumption of the i-th particles, respectively; G_o and G_p are the gas dynamic conductivities of the effusion outlet and the pipeline from the evaporation chamber to the reactor, respectively; T_s is the temperature of the vapour source; J_o is the signal intensity measured at the reactor temperature T_o, where the neglect of decomposition is possible; J is the intensity; T is the decomposition temperature; and V is the volume of the reactor.

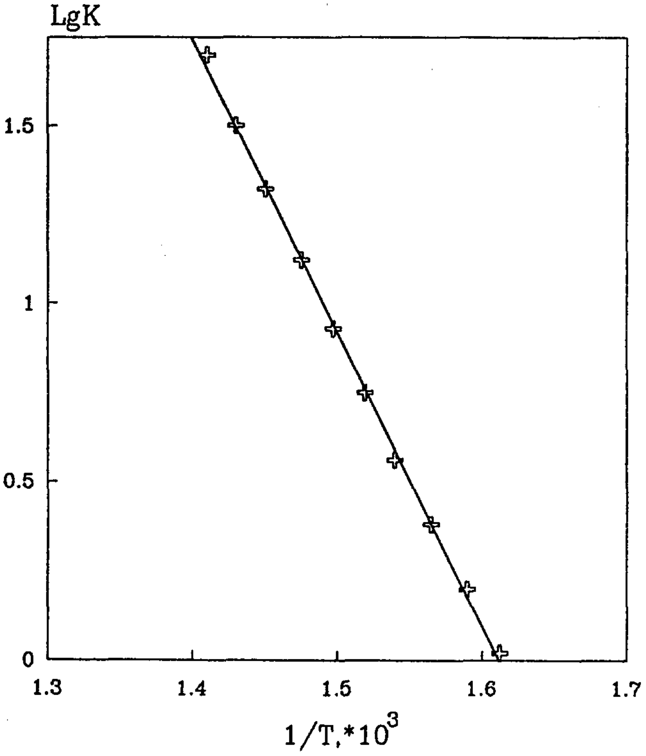

Fig. 5 Dependence of rate constant logarithm on reciprocal temperature for the thermolysis of Cu(dpm)$_2$ vapour

Taking into account the data from [10] concerning the behaviour of metal β-diketonates in the gas phase, it is possible to neglect the rate of formation of the initial particles. If it is assumed that the time for establishment of stationary reaction conditions is much shorter than the time during which temperature variations may be neglected, and if a first-order reaction is assumed for the initial component, the effective rate constants for Cu(dpm)$_2$ vapour decomposition can be calculated by using the equation:

$$K = (G_o + G_p)\cdot[(T_s\cdot T_o)^{1/2}/T)\cdot J_o - J]/J\cdot V$$

From the temperature dependence of the reaction rate constant (Fig. 5), the calculated effective activation energy of the process is E_a=37.2±1.6 kcal/mol, and the preexponential factor from the Arrhenius equation is $K_o=1.5\cdot10^{13}$ s^{-1}.

Thermolysis of Cu(dpm)$_2$ vapour in oxygen

Figure 6 shows the temperature dependence of the intensities of ion peaks characterizing the variation in gas-phase composition during the reaction of Cu(dpm)$_2$ vapour with oxygen. It is seen that the presence of oxygen significantly lowers the temperature of complex decomposition (by approximately 50 deg) and affects the composition of the gas phase. In the present case the intensity of the [Cu(dpm)$_2$-2C(CH$_3$)$_3$]$^+$ ion peak (Fig. 6), which characterizes the concentration of the complex under study at the outlet of the reaction zone, quickly diminishes from a temperature of 280°±10°C.

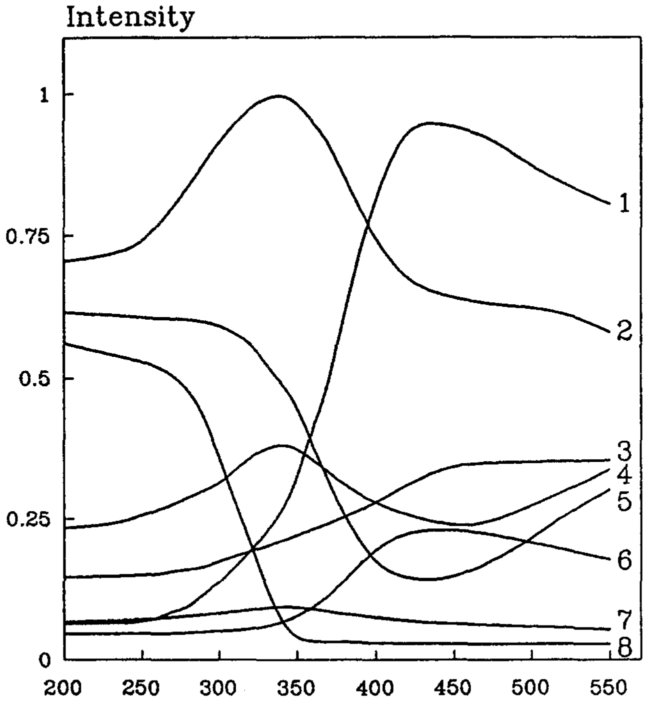

Fig. 6 Temperature dependence of ion peak intensities corresponding to the main products of thermal decomposition of copper(II) bis(dipivaloylmethanate) vapour in oxygen atmosphere: [CO$_2$]$^+$ (1), [C$_3$H$_2$O$_2$C(CH$_3$)$_3$]$^+$ (2), [CO]$^+$ (3), [C(CH$_3$)$_3$]$^+$ (4), [O$_2$]$^+$ (5), [H$_2$O]$^+$ (6), [Hdpm]$^+$ (7), [Cu(dpm)$_2$–2C(CH$_3$)$_3$]$^+$ (8)

Besides the increased intensities of ion peaks (Fig. 6) characteristic of the free ligand (in this case $Hdpm^+$ and $[C_3H_2O_2C(CH_3)_3]^+$, water, carbon monoxide and carbon dioxide are present to a significant extent among the reaction products. The maximum intensities of the peaks characteristic of the ligand are observed at 340°C, with a subsequent sharp decay. Simultaneously, a further, steeper increase in the yield of reaction products lighter than the ligand, was observed, as evidenced by the behaviour of the intensities of the $[H_2O]^+$, $[CO]^+$ and $[CO_2]^+$ ion peaks in Fig. 6. Such behaviour of the ion peak intensities points to the fact that free ligand formed on $Cu(dpm)_2$ decomposition starts to react with oxygen at temperatures above 340°C. In this case, water, carbon monoxide and carbon dioxide are formed, the latter in greatest amount. The behaviour of the oxygen peak intensity in Fig. 6 is evidence of this fact; the intensity of this peak starts to diminish sharply at temperatures above 340°C.

It is extremely interesting that the intensity of the oxygen peak starts to decrease significantly at a temperature higher than that for the intensity of the peaks of metal-containing ions, though the presence of oxygen in the reaction

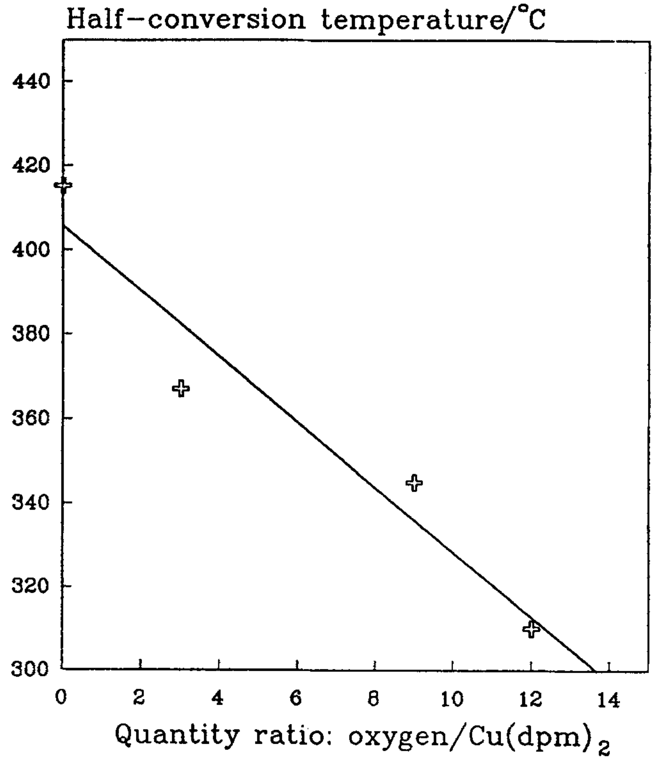

Fig. 7 Dependence of the temperature of half-conversion of $Cu(dpm)_2$ vapour on the relative content of oxygen at the inlet to the reaction zone

chamber leads to a significant (50 deg) drop in temperature of the start of $Cu(dpm)_2$ vapour decomposition. This points to the catalytic character of the thermolysis of $Cu(dpm)_2$ vapour in the presence of oxygen.

Attention should also be paid to the behaviour of the oxygen ($M/Z=32$) when its amount is maximum during the conducted experiments; this case is presented in Fig. 6. Minimum intensity is observed at a temperature near 425°C, and the intensity then begins to increase. It is possible to explain such behaviour only by assuming variation of the reaction mechanism stipulated by the kinetic peculiarities of the process, and consequently variation of the composition of the gaseous products.

Analysis of the full spectrum at different temperatures, and the temperature dependence, suggests formation of the oxygen-saturated particle $C_2H_2O_2$ (glyoxal, 57 M/Z) at temperatures above 425°C during the intermediate stage of $Cu(dpm)_2$ decomposition. In this temperature range, the maximum in the curve is observed, corresponding to carbon dioxide, and the minimum in the oxygen curve. In this case the intensity of the peak $M/Z=28$ continues to increase slowly with temperature. It is possible to explain this growth by the presence of the fragment CO^+ during the ionization of the species assumed to be formed as result of oxidation of the coordinated ligand. During the experiments with a lower oxygen amount in the reaction zone, we did not observe the maximum in the curve for carbon dioxide or the minimum oxygen curve in the temperature range above 400C. There was a steadily increasing dependence.

The temperature above which the sharp drop in the curve of the variation of the amount of initial molecules in the reaction zone is observed is practically independent of the ratio of the components in the mixture.

Experiments performed under various conditions showed that the qualitative composition of the products is weakly dependent on the ratio of oxygen and $Cu(dpm)_2$ vapour. This ratio strongly affects the rate of the reaction, which increases with increase of the relative oxygen concentration in the reaction zone. Figure 7 shows the dependence of the half-conversion temperature (when the intensity of the molecular peak diminishes two-fold) on the relative oxygen content in the bulk.

Thermolysis of Hdpm vapour

The gas-phase thermal stability of Hdpm vapour in vacuum and in oxygen medium was investigated to obtain a more reliable interpretation of the results of $Cu(dpm)_2$ thermolysis under various conditions and to prove certain assumptions. The results of these experiments are presented in Figs 8 and 9. The data indicate that the thermal stability of the ligand is significantly lower in the presence of oxygen. In Fig. 8, a noteworthy decrease in ligand peak intensities ($[Hdpm]^+$, $[C_3H_2O_2C(CH_3)_3]^+$, $[C(CH_3)_3]^+$ and $[C_2H_3O]^+$) starts at 590°±10°C, though the increase in intensity of the $[C_2HO]^+$ ion peak is observed at ca. 500°C (this corresponds to the main product of ligand vapour thermolysis), whereas in Fig. 9 the decay in the Hdpm peak intensities occurs even at 320°±10°C, with carbon dioxide as the main product (in the sense of quantity) of ligand vapour oxidation.

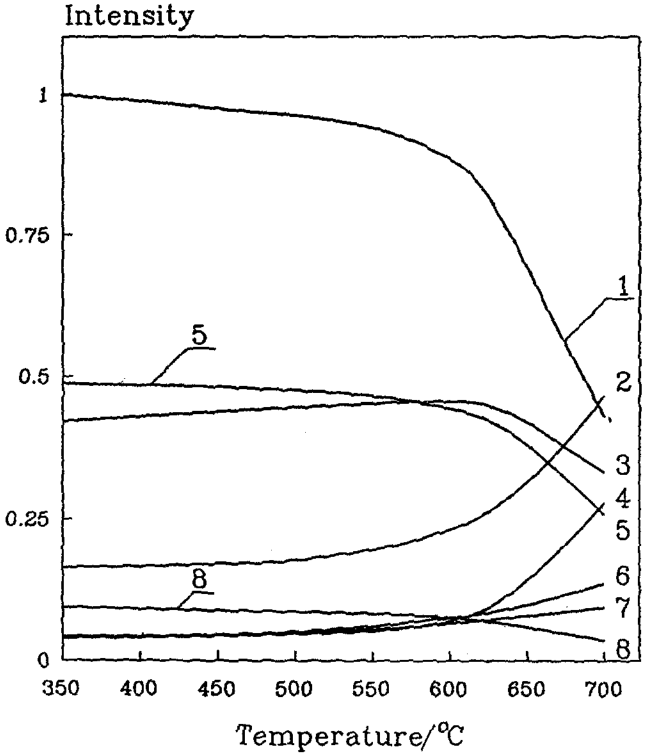

Fig. 8 Temperature dependence of ion peak intensities corresponding to the main products of thermal decomposition of Hdpm vapour: $[C_3H_2O_2C(CH_3)_3]^+$ (1), $[C_2HO]^+$ (2), $[C(CH_3)_3]^+$ (3), $[CO]^+$ (4), $[C_2H_3O]^+$ (5), $[CO_2]^+$ (6), $[H_2O]^+$ (7), $[Hdpm]^+$ (8)

The initial stage of Hdpm decomposition involves the abstraction of a water molecule, with the formation of $C(CH_3)COCHC_5H_8$, the corresponding peaks having mass numbers M/Z=18 and 166, respectively. With the increase of temperature, this organic species decomposes, eliminating methyl and ethyl radicals, and giving rise to fragments 151 M/Z and 137 M/Z. The latter decomposes with the formation of C_4H_4O, which leads to a peak 67 M/Z for $[C_4H_4O]^+$, and a wide variety of hydrocarbon particles. All oxygen-containing species undergo fragmentation, with $[C_2HO]^+$ ion formation (41 M/Z), $[CO]^+$ (28 M/Z), maximum for all particles. The intensities of peaks corresponding to the molecular ions of the above-mentioned products are very weak. Therefore, Fig. 8 shows the curves for $[C_2HO]^+$ and $[CO]^+$, which describe the total variation in oxygen-containing products.

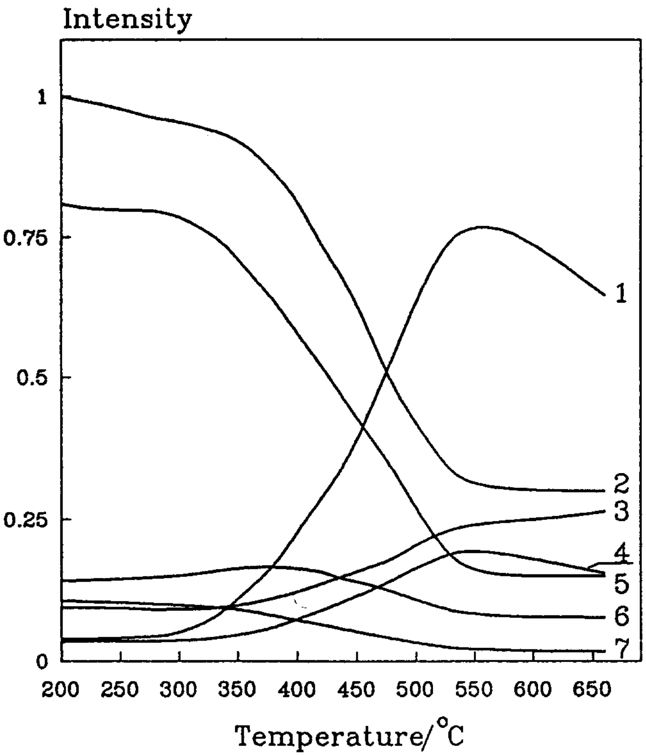

Fig. 9 Temperature dependence of ion peak intensities corresponding to the main products of thermal decomposition of Hdpm vapour in oxygen: $[CO_2]^+$ (1), $[O_2]^+$ (2), $[CO]^+$ (3), $[H_2O]^+$ (4), $[C_3H_2O_2C(CH_3)_3]^+$ (5), $[C(CH_3)_3]^+$ (6), $[Hdpm]^+$ (7)

The results on the thermal stability of ligand vapour without oxygen and in its mixtures with oxygen are in good agreement and accord with the interpretation of the data on the thermolysis of $Cu(dpm)_2$ vapour presented in Figs 4 and 6. Thus, for example the peak intensity maxima relating to the free ligand (at 340°C in Fig. 6) are explained simply by its decomposition in the presence of oxygen.

Conclusions

Analysis of the temperature dependence of the gas-phase decomposition of $Cu(dpm)_2$ vapour under different conditions points primarily to the significant influence of oxygen. In the absence of oxygen, the threshold of the stability of

Cu(dpm)$_2$ is 330°±10°C, whereas in the presence of oxygen it is 280°±10°C. The reaction products also change. In both cases, the main product of reaction in the initial stages of decomposition is Hdpm, but the thermolysis of Cu(dpm)$_2$ vapour in its mixtures with oxygen at temperatures above 330°C results in ligand oxidation products due to the low thermal stability of the ligand in oxygen. Oxygen is practically not consumed in the thermolysis of Cu(dpm)$_2$ vapour before oxidation of the ligand. This is evidence of the catalytic character of the reaction.

Increase of the oxygen content of the gas mixture does not change the qualitative composition of the products of thermolysis of Cu(dpm)$_2$ vapour, but leads to a higher reaction rate.

As concerns the use of Cu(dpm)$_2$ in the synthesis of high-temperature superconducting films by means of the CVD method, this complex is clearly of great promise especially for low-temperature processes in mixtures with oxygen within the temperature range 350°–400°C.

Our next work will involve an investigation of the thermolysis of Y(dpm)$_3$ vapour.

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Zusammenfassung — Unter Verwendung einer Zweitemperaturenvariante der Knudsenschen Doppelkammerzelle wurde mittels MS-Untersuchung der Gasphasenzusammensetzung im Temperaturbereich 150°-550°C der thermische Abbau von Kupfer(II)-bis(dipivaloylmethanat) (Cu(dpm)$_2$) untersucht. Es wurde der Temperaturbereich für die Stabilität der gasförmigen Komplexe in Vakuum sowie in Gemischen mit Sauerstoff in verschiedenen Verhältnissen bestimmt. Dabei wurde die Temperaturabhängigkeit der Geschwindigkeitskonstante für die Thermolyse von Cu(dpm)$_2$ ermittelt. Weiterhin wurde die thermische Stabilität von Hdpm-Dampf sowie der Einfluß von Sauerstoff auf die Thermolyse der Liganden bestimmt.