MASS SPECTROMETRIC STUDY OF GAS-PHASE THERMAL STABILITY OF YTTRIUM(III) TRIS(DIPIVALOYLMETHANATE)

A. F. Bykov, P. P. Semyannikov and I. K. Igumenov

INSTITUTE OF INORGANIC CHEMISTRY, NOVOSIBIRSK-90, 630090 RUSSIA

The processes of thermal decomposition of yttrium(III) tris(dipivaloylmethanate) (Y(dpm)₃) vapour and its mixtures with oxygen were investigated by using the two-temperature variant of the double-chamber Knudsen cell, with mass spectrometric recording of the gas-phase composition within the temperature range 150°–650°C. The threshold temperatures of the stability of the complex vapour were determined. The temperature dependence of the rate constant was obtained for the thermolysis of Y(dpm)₃ vapour, and the effective activation energy of the process was determined. Qualitative data were obtained on the influence of Cu(dpm)₂ vapour on the thermolysis of Y(dpm)₃ vapour in oxygen atmosphere.

Keywords: kinetic parameters, mass spectrometry, superconducting films, thermal stability, yttrium(III) tris(dipivaloylmethanate)

Introduction

Numerous recent publications are indicative of the successful application of β-diketonates of such metals as yttrium, barium, copper, etc, as initial reagents for HTSC film preparation by the MO CVD method [1, 2]. This success is mainly limited by the use of precision equipment for the method of chemical deposition from the gas phase. However, the literature lacks data on the volatility, stability and chemical features of the compounds applied. In fact, only data on the volatility of copper complexes [3] and contradictory data on the volatility of yttrium(III) tris(dipivaloylmethanate) (Y(dpm)₃) are available [4, 5]. There is no information on the volatility of barium(II) β-diketonates or on the thermal stability of the vapour of metal complexes used for the preparation of superconducting films.

We recently reported [6] the thermolysis of Cu(dpm)₂ and Hdpm vapour under different conditions, using the same method. The system of injection of the vapour of the substances under study was described in detail. The results of that

work have been used for data analysis and in a number of the conclusions in the present publications.

Experimental

The work was done with an automated time-of-flight MSKh-6 (USSR) mass spectrometer with a mass recording range of 13000 M/Z and a resolution of 350 at 50% of the peak height. The system of injection of the vapour of the substance under study is a specialized, two-temperature variant of the double-chamber Knudsen cell, with molecular flow modulation at the effusion outlet. The volatile compound under study in a quartz container (or two substances in separate containers in the case of the co-vaporization of $Y(dpm)_3$ and $Cu(dpm)_2$ was placed in a separate vaporization chamber, which was evacuated, and heated to the temperature necessary for substance transport to the reaction zone. When necessary, the gas reagent was added to the substance vapour at the reaction zone inlet, and its influence on the thermolysis was studied. The gas-phase composition at the outlet from the reaction zone was determined mass spectrometrically. The whole system has been described in detail in [6].

The thermal stability of $Y(dpm)_3$ under various conditions was studied via the temperature dependence of the peak intensities of ions from the mass spectra of the vapour of the substance under study, the products of its thermolysis and reaction additives. Under real-time conditions, it was possible to trace the intensities of 20 peaks in the mass spectrum simultaneously. The temperature sweep in the reaction zone was 2.5 deg/min. We checked the coincidence of the direct (in the direction of temperature increase) and reverse behaviour of the dependence of ion peak intensities.

$Y(dpm)_3$ was investigated in vaporization chamber at temperatures of $110°$–$140°C$ which corresponds to a saturated vapour pressure of from $1 \cdot 10^{-3}$ to $2.6 \cdot 10^{-2}$ Torr, taking into account the data from [3], approximated over the low-temperature range. Investigations of the interaction with oxygen involved a 550-fold excess of oxygen relative to $Y(dpm)_3$. Calculations were carried out with theoretical values of ionization cross-sections and the additivity law [7]. The gas-phase decomposition was studied in the temperature range $150°$–$650°C$.

Results and discussion

Mass spectrum of Y(dpm)₃

Figure 1 shows the mass spectrum of $Y(dpm)_3$, which is mainly comprised of peaks of metal-containing ions, the most intensive among them being $[Y(dpm)_2]^+$,

followed by $[Y(dpm)_3C(CH_3)_3]^+$ and $[Y(dpm)_3]^+$, with mass numbers $M/Z=455$, 581 and 638. This indicates that this compound is a monomer in the gas phase. The abstraction of ligands and substituents from the molecules of trivalent metal β-diketonates during electron impact is a rather typical phenomenon [8], but investigation of this is not included in the present report. The fragmentation character of $Y(dpm)_3$ is closest to that of acetylacetonate complexes. A distinctive feature is the absence of metal ions and oxides in the mass spectrum.
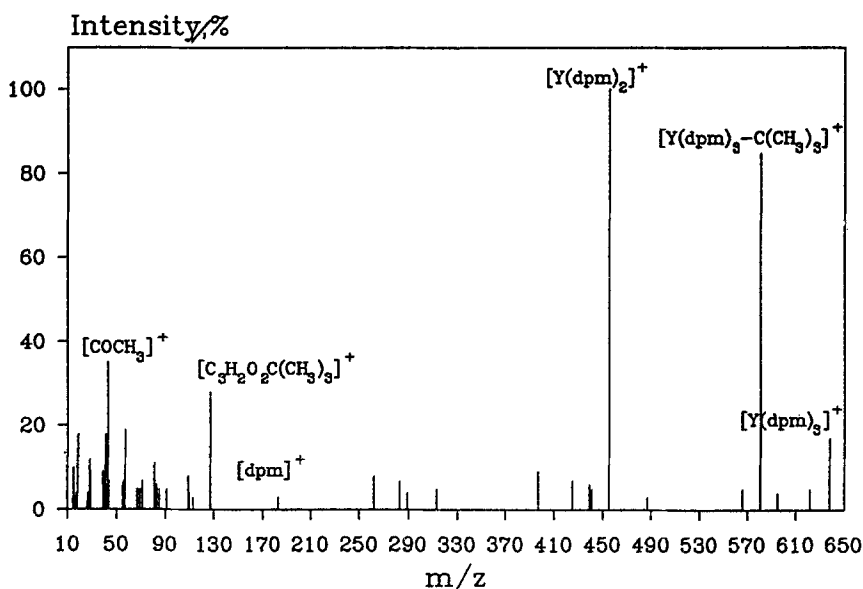

Fig. 1 Mass spectrum of yttrium(III) tris(dipivaloylmethanate)

Thermolysis of Y(dpm)₃ vapour

Figure 2 shows curves characterizing the variation in gas-phase composition with temperature during the decomposition of $Y(dpm)_3$. This Figure, and also the subsequent ones, give information on the integral intensities (squares under peak envelope) of the ion peaks in arbitrary units.

The decrease in intensity of the peaks of metal-containing ions $[Y(dpm)_3]^+$, $[Y(dpm)_3C(CH_3)_3]^+$ and $[Y(dpm)_2]^+$ at $490°\pm10°C$ in Fig. 2 is an indication of the beginning of thermal degradation of $Y(dpm)_3$ vapour. The threshold temperatures were determined from the temperature dependence of the intensities of the ion peaks in the mass spectrum under study. In turn, the spectral changes of light (not containing metal) species indicate that hydrocarbon fragments of Hdpm are the

main products of thermolysis. The behaviour of the peaks characteristic of the ligand [6] ($[C_3H_2O_2C(CH_3)_3]^+$, M/Z=127; $C_2H_3O^+$, M/Z=43 and the ligand radical, M/Z=183, not shown in Fig. 2), whose intensities are practically constant with temperature, points to the presence of two opposite processes: ligand formation in the thermolysis of $Y(dpm)_3$, and destruction of the ligand at a given temperature. The information on the thermal stability of Hdpm is a basis for this assumption [6].
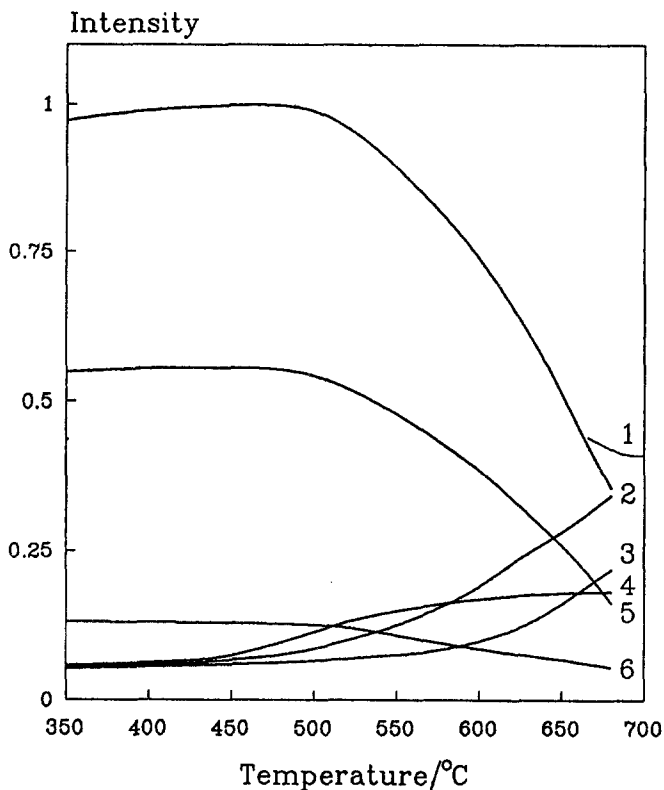

Fig. 2 Temperature dependence of ion peak intensities corresponding to main products of thermal destruction of yttrium(III) tris(dipivaloylmethanate) vapour: $[Y(dpm)_2]^+$ (1), $[C_2HO]^+$ (2), $[CO]^+$ (3), $[C(CH_3)_3]^+$ (4), $[Y(dpm)_3–C(CH_3)_3]^+$ (5), $[Y(dpm)_3]^+$ (6).

Kinetic parameters of thermolysis of Y(dpm)₃ vapour

From the data on the irreversibility of the gas-phase thermolysis of volatile metal β-diketonates [9], assuming first-order kinetics for the thermolysis of $Y(dpm)_3$ vapour, the reaction equation [9] was used to calculate the temperature dependence of the reactor rate constant, which is shown in Fig. 3. In conformity

with this dependence, the effective activation energy and preexponential factor of the Arrhenius equation were calculated for the vapour thermolysis: E_a=34.3±2.0 kcal/mol, K_o=2.2·10^9 s^{-1}.

Thermolysis of Y(dpm)₃ vapour in oxygen atmosphere

The thermolysis of Y(dpm)₃ vapour in oxygen is of interest, because the processes of HTSC film preparation are as a rule carried out in the presence of oxygen in the reaction zone. Figure 4 presents information on the variation in the gas-phase decomposition of mixtures of Y(dpm)₃ vapour with oxygen, depending on the reactor temperature. In oxygen, there is a sharp decrease in thermal stability of the complex under study. This is clearly seen from a comparative analysis of Figs 2 and 4. The starting temperature of the decrease in intensity of metal-containing peaks (Fig. 4) is shifted to the left by ca. 95 deg. The change in the location of the inflection in the temperature curves of the [Y(dpm)₂]$^+$ and
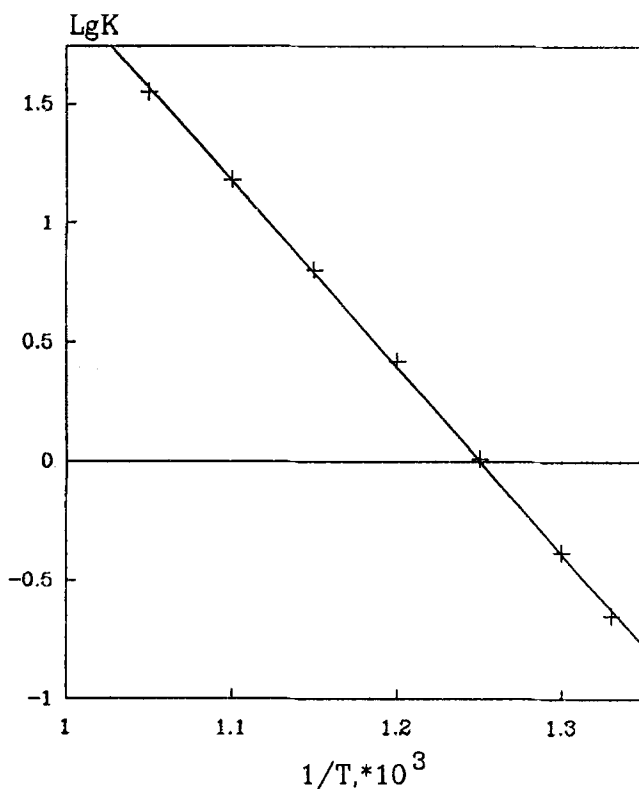

Fig. 3 Dependence of logarithm of reaction rate constant for thermolysis of yttrium(III) tris(dipivaloylmethanate) vapour on reciprocal temperature

$[Y(dpm)_3C(CH_3)_3]^+$ ion peak intensities (characterizing the threshold of thermal stability) is evidence of this. For the thermolysis of $Y(dpm)_3$ vapour in oxygen, the threshold of thermal stability is ca. $395°C$.

There are two further characteristic features: the good reproducibility of the inflection in the temperature dependence of metal-containing ions at the different oxygen concentrations in the mixture $(395°\pm5°C)$; and an increase in slope of the curves with increasing oxygen content is observed, as evidence of a reaction rate increase.
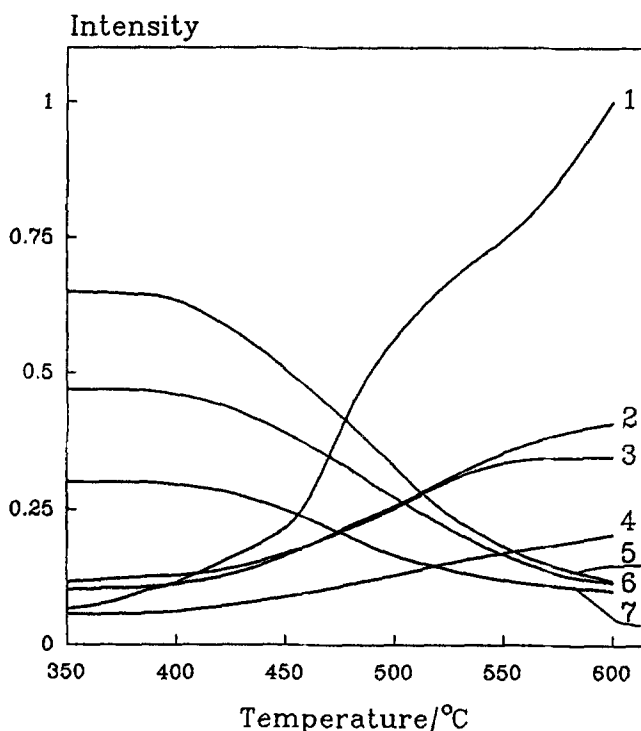

Fig. 4 Temperature dependence of ion peak intensities corresponding to the main products of thermal destruction of yttrium(III) tris(dipivaloylmethanate) vapour in oxygen: $[CO_2]^+$ (1), $[C_2HO]^+$ (2), $[CO]^+$ (3), $[C(CH_3)_3]^+$ (4), $[O_2]^+$ (5), $[Y(dpm)_2]^+$ (6), $[Y(dpm)_3-C(CH_3)_3]^+$ (7)

Carbon dioxide ($M/Z=44$) and carbon monoxide ($M/Z=28$) are the main reaction products in oxygen, the fraction of the latter being greater than in the decomposition of $Y(dpm)_3$ vapour without oxygen. Since the thermal stability of the ligand is lower than that of $Y(dpm)_3$ in oxygen, the appearance of carbon dioxide and carbon monoxide among the thermolysis products is quite natural: they result from ligand thermolysis in oxygen [6].

Combined thermolysis of Y(dpm)₃ and Cu(dpm)₂ in oxygen

High-temperature superconducting systems are usually multicomponent. As a rule, a mixture of complexes in an oxygen atmosphere is present in the process of high-temperature ceramic film deposition.

There is no possibility for us to study the thermolysis in the whole multicomponent system with a mass spectrometer, and therefore, the thermolysis of $Y(dpm)_3$ and $Cu(dpm)_2$ vapour in oxygen has been investigated with the system available. Since the difference between the vapour pressures of the complexes is less than one order of magnitude [3, 4], it is possible to vaporize both components at the same temperature, which in the present experiments was 120°C. The ratio of the concentrations of the components calculated from the maximum ionization cross-sections using the additivity law [7] was 7.5 for $Cu(dpm)_2/Y(dpm)_3$.

Figure 5 shows curves for the thermal decomposition of mixtures of $Y(dpm)_3$ and $Cu(dpm)_2$ in oxygen. Information is presented on the most intensive peaks of metal-containing ions for each complex: $[Cu(dpm)_2 \cdot 2C(CH_3)_3]^+$ ($M/Z=315$) for $Cu(dpm)_2$, and $[Y(dpm)_2]^+$ ($M/Z=455$) for $Y(dpm)_3$. For convenience, the intensity of the latter is 3 times greater in Fig. 5 in comparison with the intensities of the other peaks. Figure 5 also presents information on the products of thermolysis of both components. The situation is more complex because these products are similar for both initial reagents, because they contain the same organic ligand. On the other hand, this condition simplifies the whole picture of the process, since it excludes the formation of new complexes in the gas-phase due to ligand exchange. In the mass spectrum of the mixture of the two complexes, the formation of new chemical compounds containing various metal atoms was not observed.

The curves in Fig. 5 yield evidence of the mutual influence of the components of the mixture. The process starts with the thermal destruction of $Cu(dpm)_2$ vapour at 280°±10°C, this temperature being characteristic for this complex in its mixture with oxygen [6]. The decrease in $[Cu(dpm)_2 \cdot 2C(CH_3)_3]^+$ ion peak intensity is evidence of this. The simultaneous increase in $[C_3H_2O_2C(CH_3)_3]^+$ peak intensity is characteristic for the mass spectrum of Hdpm. It was shown earlier that this ligand is a primary product of $Cu(dpm)_2$ vapour thermolysis. The maximum in the intensity curve of the $[C_3H_2O_2C(CH_3)_3]^+$ ion peak and a decrease in oxygen peak intensity are observed with the approach to the threshold of thermal stability of the ligand vapour (320°±10°C). Almost simultaneously, a decrease in $[Y(dpm)_2]^+$ ion peak intensity is observed, which characterizes the vapour concentration of the yttrium complex. This is quite natural for its behaviour in oxygen, in accordance with the results in Fig. 4. Thus, the behaviour of the curves from Fig. 5 up to ca. 420°C is evidence of simultaneous processes of thermolysis of $Y(dpm)_3$ and $Cu(dpm)_2$ in oxygen.

However, from 420°C a completely different picture is observed. The behaviour of the $[Y(dpm)_2]^+$ ion peak intensity curve in this temperature range in Fig. 5 unambiguously points to a decrease in the rate of thermolysis of $Y(dpm)_3$

vapour. Opposite behaviour is exhibited by the $[C_2HO]^+$ ion peak, which is characteristic for the products of thermolysis of both complexes under study. In our opinion, such a decrease in the rate of thermolysis of $Y(dpm)_3$ vapour may be explained by the drop in oxygen concentration in the reaction zone due to $Cu(dpm)_2$ vapour thermolysis in oxygen. Moreover, $Y(dpm)_3$ "loses" the competition for oxygen due to its lower rate of thermolysis relative to that of $Cu(dpm)_2$ at the same temperature.
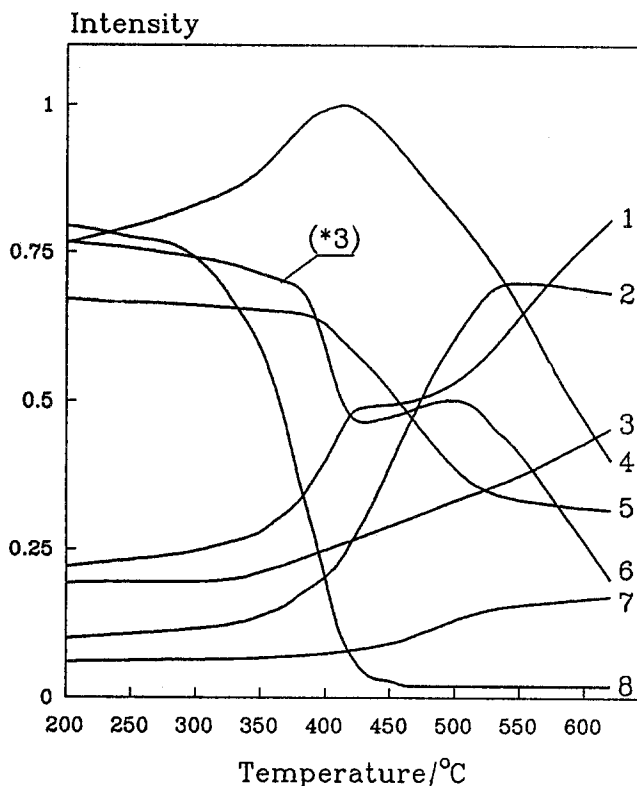

Fig. 5 Temperature dependence of ion peak intensities corresponding to main products of combined thermolysis of yttrium(III) and copper(II) dipivaloylmethanates in oxygen: $[C_2HO]^+$ (1), $[CO_2]^+$ (2), $[CO]^+$ (3), $[C_3H_2O_2C(CH_3)_3]^+$ (4), $[O_2]^+$ (5), $[Y(dpm)_2]^+$ (6), $[H_2O]^+$ (7), $[Cu(dpm)_2-2C(CH_3)_3]^+$ (8)

The result of such a "loss" is the rise in $[Y(dpm)_2]^+$ ion peak intensity in the temperature range from 420° to 500°C, which is indicative of the deceleration and cessation of the thermolysis of $Y(dpm)_3$ vapour. The following decrease in $[Y(dpm)_2]^+$ ion peak intensity at temperatures above 500°C (Fig. 5) indicates the beginning of thermolysis of $Y(dpm)_3$ vapour without additives.

It is possible to establish the influence of Cu(dpm)$_2$ vapour in the presence of oxygen. This influence is connected with the conditions created during the thermolysis of Cu(dpm)$_2$ vapour in oxygen (oxygen impoverishment of the reaction zone), which increases the thermal stability of Y(dpm)$_3$ vapour up to the level of its own stability (without oxygen).

Conclusions

It has been shown that the threshold of Y(dpm)$_3$ vapour stability is extended up to 490°±10°C. The influence of oxygen on the thermolysis process results in a decrease in the thermal stability of the complex vapour to 395°±5°C. The main gaseous reaction products in the absence of oxygen are fragments of organic ligands of the complex molecules, while in the presence of oxygen they are the oxidation products of these fragments, the most abundant among them being carbon monoxide and carbon dioxide.

Variation of the proportions of the complex vapour and oxygen does not influence the qualitative composition of the reaction products, but leads to a changed reaction rate, which increases with increasing reagent concentration in the reaction zone.

The influence of Cu(dpm)$_2$ vapour on the thermolysis of Y(dpm)$_3$ vapour in oxygen has been found. Since Cu(dpm)$_2$ vapour has a lower thermal stability than that of Y(dpm)$_3$, conditions of an oxygen deficit for the thermolysis of Y(dpm)$_3$ are created in the reaction zone. This leads to an increase in its thermal stability up to the values characteristic for the conditions in the absence of oxygen.

Application of Y(dpm)$_3$ in CVD processes is possible at relatively high temperatures (greater than 500°C) due to its high (as compared with metal β-diketonates) thermal stability and relatively low rate of thermolysis. The presence of Cu(dpm)$_2$ vapour in the process of film preparation greatly facilitates this. Evidently, the temperature range above 600°C is the most acceptable from the point of view of Y(dpm)$_3$ growth rates.

References

1 A. J. Parson, R. G. Charles, D. N. Schmidt, J. R. Szedon, G. J. Machiko and A. I. Braginski, Appl. Phys. Lett., 53 (1988) 1756.
2 T. Tsurioka, H. Takanashi, R. Kawasaki and T. Kanamori, Appl. Phys. Lett., 54 (1989) 1808)
3 Yu. P. Chumachenko, Ph.D. Thesis, Institute of Inorganic Chemistry, Novosibirsk 1979 (in Russian)
4 J. E. Sire et al., J. Amer. Chem. Soc., 91 (1969) 3476.
5 S. G. Konstantinov et al., Theoretical and Applied Chemistry of Metal β-Diketonates, Nauka, Moscow 1985, p. 148 (in Russian).
6 A. F. Bykov, P. P. Semyannikov, I. K. Igumenov, J. Thermal Anal., (in press).
7 J. M. Otwos and D. P. Stewenson, J. Amer. Chem. Soc., 78 (1956) 536.

8 N. V. Gerbeleu and K. M. Indricean, Mass Spectrometry of Coordination Compounds, Stiinta, Kishinev 1984, p. 44.
9 P. P. Semyannikov, Ph.D. Thesis, Institute of Inorganic Chemistry, Novosibirsk 1988.

Zusammenfassung — Unter Verwendung einer Zweitemperaturenvariante der Knudsenschen Doppelkammerzelle wurde mittels MS-Untersuchung der Gasphasenzusammensetzung im Temperaturbereich 150°-650°C der thermische Abbau von Yttrium(III)-tris(dipivaloyl-methanat) (Y(dpm)$_3$) untersucht. Dabei wurden die Schwellentemperaturen der Stabilität des Komplex-Dampfes ermittelt. Für die Thermolyse des Y(dpm)$_3$-Dampfes wurde die Temperaturabhängigkeit der Geschwindigkeitskonstante sowie die effektive Aktivierungsenergie des Prozesses bestimmt. Die qualitativen Angaben wurden anhand des Einflusses von Cu(dpm)$_2$-Dampf auf die Thermolyse von Y(dpm)$_3$ in Sauerstoffatmosphäre erhalten.