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INVESTIGATION OF THERMAL PROPERTIES OF RUTHENIUM(III) β-DIKETONATE PRECURSORS FOR PREPARATION OF RuO_2 FILMS BY CVD

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Abstract

By means of a tensimetric flow method and a static method with a silica-membrane zero gauge, the dependence of vapour pressure on temperature was obtained for tris(2,4-pentanedionato)ruthenium(III), $Ru(aa)_3$, and tris(1,1,1-trifluoropentane-2,4-dionato)ruthenium(III), $Ru(tfa)_3$. The thermodynamic characteristics of vaporization and sublimation of these complexes were determined. The processes of thermal decomposition of the vapour of the compounds in vacuum, hydrogen and oxygen were investigated by using mass spectrometry in the temperature range 170–550°C for $Ru(aa)_3$ and 150–620°C for $Ru(tfa)_3$. The threshold temperatures of the stability of the vapour of the complexes and the rate constants of the thermolysis processes were determined. The main gaseous products of the thermal decomposition and the dependences of their composition on the presence of hydrogen and oxygen were established.

Keywords: CVD, ruthenium β-diketonates, thermal stability, vapour pressure

Introduction

As a material, RuO_2 is primarily characterized by high chemical stability, low volatility in comparison with oxides of other noble metals, and high conductivity. The high conductivity is well known and is applied in the manufacturing of modern thin-film resistors [1].

The formation of RuO_2 films is currently of interest because of their applications as a buffer layer between a silicon substrate and HTSC film [2], as well as a material of electrical contacts for HTSC [3]. Such films have been obtained by a method of reactive magnetron sputtering. They have high conductivity and provide a perfect diffusion barrier at minimum thickness (10–300 nm). Mention should be made of one further important property of RuO_2 films: their optical transparency in the visible and UV ranges [4].

All this testifies to an opportunity for a significant expansion of the field of application of films and materials based on RuO_2 in the near future.

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Among methods for the formation of RuO_2 films, there are advantages to the CVD method, which has recently appreciably expanded the application borders. This method yields uniform films and large rates of growth at minimum costs [5, 6]; ruthenium(III) β-diketonates and ruthenocene were used as precursors.

Optimum utilization of the advantages of the CVD method assumes the availability of knowledge about the thermal properties of volatile precursors. As a rule, this includes knowledge of the temperature dependence of the saturated vapour pressure and the thermal stability in the condensed and gas phases. Though information on the saturated vapour pressure and stability in the condensed phase is known for a limited number of precursors, research into the thermal stability of the vapour and gaseous products of reaction is practically unavailable in the literature. This generally causes the choice of non-optimal conditions for the preparation of the films.

The precursors potentially suitable for the CVD of RuO_2 and Ru films are ruthenium carbonyls, ruthenium carbonyl halides, ruthenocene, ruthenium β-diketonates and some of their organic and coordination derivatives [7]. However, the thermal decompositions of ruthenium carbonyl and ruthenium carbonyl chlorides, like those of the analogous platinum metal derivatives, are accompanied by severe corrosion of the equipment and the support materials. Further, the majority of these ruthenium compounds are moisture- and oxygen-sensitive. Ruthenocene, $(C_5H_5)_2Ru$, is the most promising compound for the formation of ruthenium films.

The thermal decomposition of ruthenocene has been studied by means of a static tensimetric method [8]. It was established by mass spectrometry that the vapour of ruthenocene contains dimeric molecules. However, the products of ruthenocene thermolysis were not investigated. Attention was first drawn to the possibility of formation of high-purity ruthenium (99.99%) *via* ruthenocene decomposition in a hydrogen atmosphere in 1964 [9]. In an oxygen atmosphere, mixed Ru–RuO_2 films were formed [5].

Metal β-diketonates are more suitable for the preparation of films and coatings of RuO_2, because the complexes already contain the necessary Ru–O bonds. However, Ru(III) β-diketonates have been less investigated then ruthenocene. A patent for the preparation of Ru films on various substrates is known, with the use of tris(2,4-pentanedionato)ruthenium(III), $Ru(aa)_3$, and tris(1,1,1-trifluoropentane-2,4-dionato)ruthenium(III), $Ru(tfa)_3$, as precursors [10].

The authors have investigated the vaporization and the thermal decomposition of the vapour of ruthenium(III) β-diketonates, which can be used in CVD processes for the preparation in particular of films of RuO_2. As subjects of investigation, $Ru(aa)_3$ and $Ru(tfa)_3$ were chosen. Research on ruthenium(III) β-diketonates in the condensed phase was described in [11].

Experimental

Synthesis

The synthesis of the complexes of Ru(III) with β-diketones was carried out according to a general method for obtaining β-diketonates of platinum metals *via* the aqua complexes [11]. The compounds were purified by zone sublimation in a vacuum gradient furnace at 5×10^{-2} Torr and 200°C for $Ru(aa)_3$, or 130°C for $Ru(tfa)_3$. The complexes were identified *via* methods of chemical analysis for C, H and F, IR spectroscopy and the melting points. The results of the chemical analyses and the melting points obtained on a Kofler hot stage are presented in Table 1.

Table 1 Results of chemical analysis of $Ru(aa)_3$ and $Ru(tfa)_3$

Compound	Content (calculated/found)/%			$T_{melt.}$/°C
	C	H	F	
$Ru(aa)_3$	45.23/43.12	5.28/5.45	–	240
$Ru(tfa)_3$	32.14/32.09	2.14/2.27	30.54/30.62	156

Vapour pressure

The density of saturated vapour above $Ru(aa)_3$ was measured with a flow method. The technique of the experiment was described in detail in [12]. A measured flow of a dry inert gas carrier (helium) was passed through a source filled with the substance. The accuracy of the maintenance of temperature was ±0.5°C, and the error in the measurement of flow rate was ±1%.

The amount of substance vaporized on the passage of a certain volume of helium was determined by weighing (the loss in mass of the substance at the source and the rise in mass of the substance in the cold zone). The two results practically coincided, i.e. the substance did not decompose in the investigated temperature interval. The pressure of saturated vapour was calculated on the assumption that the substance vaporizes in the monomolecular form. Under the conditions applied, the results obtained on the pressure of the vapour did not depend within the limits of error on the rate of helium flow (for a 4-fold change) or on the duration of the experiment. This indicated that the sublimation proceeded under quasi-equilibrium conditions (i.e. saturation was reached in the system and the influence of vapour diffusion was small).

The saturated vapour pressure of $Ru(tfa)_3$ was studied by the static method with a silica-membrane zero gauge. The technique of the experiment and the set-up were described in [13]. The obtained data were reduced to standard conditions. The errors determined from the saturated vapour pressures of naphthalene and mercury were taken into account for temperature values. The experimental data developed under the special method [14] are presented in the form $\ln P$ (bar)$=B-A/T$ in Table 2. The temperature dependence of dispersions calculated *via* the pressure equation are also listed in Table 2.

From the data on the carrying of the substance by the inert gas flow under quasi-equilibrium conditions, and the temperature dependence of the saturated vapour pressure for the investigated complexes, the thermodynamic parameters ΔH^{o}_{T} and ΔS^{o}_{T} were calculated.

Mass spectrometry

For study of the processes of thermal decomposition of the complexes $Ru(aa)_3$ and $Ru(tfa)_3$ in the gas phase, we used the system based on the MSKh-6 (USSR) time-of-flight mass spectrometer, with a mass number range up to 3000 *m/z* and a mass resolution 3×10^{-3} a.m.u. An electron-impact source was operated at 70 eV ionizing voltage. The system used for the injection of the vapour of the compounds was a two-temperature variant of the Knudsen effusion method with a double chamber. The injection system was reported earlier [15, 16], when the circuit of the experimental set-up and the experimental technique were described. The design permitted various gases to enter the reaction zone.

The thermal stabilities of $Ru(aa)_3$ and $Ru(tfa)_3$ under different conditions were studied *via* the temperature dependence of the intensities of the ion peaks in the mass spectrum of the vapour of the compound under study, and also the products of its thermolysis. Each experimental curve had 75 points. To obtain the temperature curves, the reactor was heated linearly at a rate of 1.5–2.5°C min^{-1}, starting as a rule from a temperature 5–10°C higher than the temperature of the evaporation chamber. The experiments were carried out under the conditions of the direct and reverse courses of temperature of the reactor. The pressures in the evaporation chamber, thermal reactor and analyser of the mass spectrometer did not exceed 5×10^{-2}, 1×10^{-4} and 1×10^{-6} Torr, respectively. The mode of gas flow in all parts of the system was molecular, i.e. interaction between molecules of the compound and the reaction products was practically absent.

In our experiments, the evaporation chamber temperature was 170°C for $Ru(aa)_3$ and 120°C for $Ru(tfa)_3$. In the temperature curves, only the molecular ion peaks characterized the concentration of the initial compound, because there was no difference in behaviour of metal ion peaks for the two complexes.

As an indefiniteness as concerns the conditions under which the process took place, a film resulting from thermal decomposition of the investigated complex was preliminarily formed on the walls of the reaction zone. This was important, with regard to the well-known catalytic properties of ruthenium [8]. In our experiments, the concentrations of oxygen and hydrogen exceeded the concentration of the molecules of the initial compounds by a factor of approximately 4–7.

Table 2 Thermodynamic parameters of sublimation and vaporization of $Ru(aa)_3$ and $Ru(tfa)_3$

Compound	Process	Number of points	T/ °C	$\ln P(\text{bar}) \pm \sigma = B - A/T$			ΔH°_{T}, kJ mol^{-1}	ΔS°_{T}, kJ (mol K)$^{-1}$
				B	A	σ^2		
Flow method:								
$Ru(aa)_3$	subl.	7	150–220	25.56	15228	$12404/T^2$–$53.8/T$+0.60	127.0±0.9	212.5±2.0
Silica-membrane zero gauge:								
$Ru(tfa)_3$	subl.	13	110–150	19.63	10829	$134095/T^2$–$637.0/T$+0.76	90.0±3.0	163.2±7.2
$Ru(tfa)_3$	vapor.	11	160–210	16.50	9458	$14891/T^2$–$64.2/T$+0.07	78.7±0.8	137.2±1.7

Results and discussion

Saturated vapour pressure of Ru(aa)$_3$ and Ru(tfa)$_3$

The temperature dependence of the saturated vapour pressure of each complex is shown in Fig. 1. The experimental results exhibited good reproducibility within the studied temperature range. The thermodynamic characteristics of the processes of vaporization and sublimation and their errors are listed in Table 2.

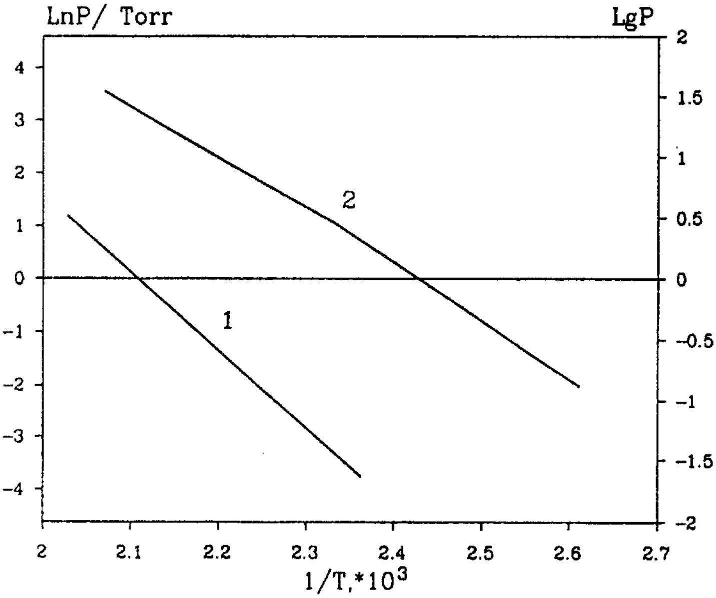

Fig. 1 Dependence of the logarithm of saturated vapour pressure on reciprocal temperature for the complexes Ru(aa)$_3$ (1) and Ru(tfa)$_3$ (2)

The obtained parameters of sublimation and vaporization were usual for metal(III) β-diketonates [17]. The increase in volatility on introduction of a trifluoromethyl group is typical for these compounds. The difference in saturated vapour pressure is also general.

In our opinion, the sublimation enthalpy for Ru(aa)$_3$ obtained by the Knudsen method [18] (145.1±2.5 kJ mol^{-1}) is somewhat high. We believe that this is characteristic for this method applied to this class of compounds.

Mass spectra of Ru(aa)$_3$ and Ru(tfa)$_3$

The mass spectra of Ru(aa)$_3$ and Ru(tfa)$_3$ were earlier reported in detail [19], together with electron beam diagrams. The mass spectra of our complexes did not display any differences. The mass spectrum of the positive ions of Ru(aa)$_3$

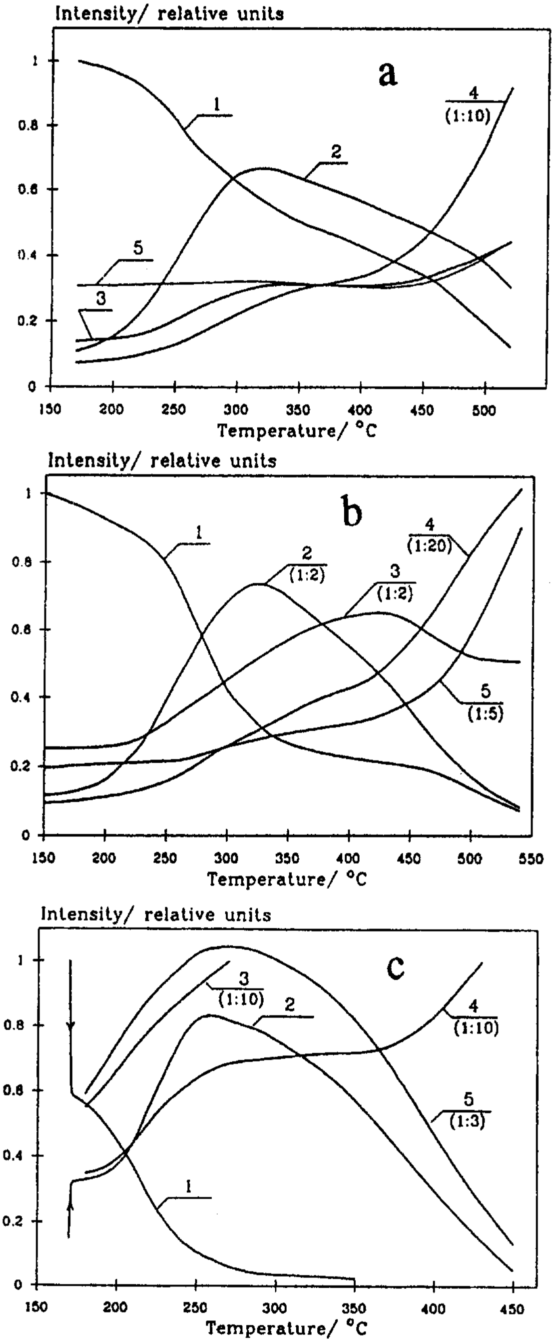

Fig. 2 Temperature dependence of intensities of ion peaks corresponding to the main gaseous products of thermal decomposition of Ru(aa)$_3$ vapour in vacuum (a), in hydrogen (b) or in oxygen (c): $[Ru(aa)_3]^+$ (1), $[Haa]^+$ (2), $[CO_2]^+$ (3), $[CO]^+$ (4), $[H_2O]^+$ (5)

is mainly comprised of three intense peaks: the molecular ion $[Ru(aa)_3]^+$ (*m/z* 399 for ^{102}Ru), $[Ru(aa)_2]^+$ (*m/z* 300) and $[CH_3CO]^+$ (*m/z* 43). The sequence of the loss of C_3H_4 from $[Ru(aa)_2]^+$ to yield $[Ru(aa)(CH_3)(CO_2)]^+$ (*m/z* 260), followed by the loss CO_2 to yield $[Ru(aa)(CH_3)]^+$ (*m/z* 216), is a relatively important reaction sequence as concerns the observation of the peaks. A number of less intense multiplets in the mass range 120–200 characterize the mass spectrum of $Ru(aa)_3$.

In our experiments, the most intense ion peak was that of $[Ru(aa)_2]^+$. The peak of the free ligand (Haa) with *m/z* 100 was observed.

The base peak in the mass spectrum of $Ru(tfa)_3$ is the metal-free peak *m/z* 43, $[CH_3CO]^+$. The most intense peak for a metal-containing ion is that of $[Ru(tfa)_2]^+$ (*m/z* 408), followed by $[Ru(tfa)_3]^+$ (*m/z* 561). In the case of $[Ru(tfa)_2]^+$, mass loss occurs, with the rapid removal of CO_2 and CF_2 accompanied by the rearrangement of F to the ruthenium ($[RuF(tfa)]^+$, *m/z* 274). A small peak of $[Ru(tfa)]^+$ is also found in the mass spectrum.

The characteristic feature of the mass spectrum of $Ru(tfa)_3$ under electron impact is the absence of a peak of the free ligand Htfa.

Thermolysis of Ru(aa)₃ vapour

Figure 2 shows the temperature dependence of the intensities of the ion peaks characterizing the change in gas phase composition on the thermolysis of ruthenium acetylacetonate vapour in vacuum (a), hydrogen (b) and oxygen (c). The presented curves reveal that in all cases (a, b, c) the initial thermal decomposition process is accompanied by elimination of the free ligand in the gas phase. This is the major gaseous product of the reaction in the temperature range up to 300–350°C. It is possible to explain the presence of the free ligand in the gaseous products of thermal decomposition if the dehydrogenation of the molecule of the complex with homolytic cleavage of the metal–ligand bond is assumed.

The products of decomposition of the molecules of the initial complex begin to increase appreciably at temperatures higher than 400°C and they prevail in the mass spectrum at 500°C. They are mainly CO, CO_2 and H_2O.

Hydrogen

The distinctive feature of the thermolysis of $Ru(aa)_3$ in the presence of hydrogen is the somewhat higher temperature of initial decomposition (by approximately 10°C for the same accuracy of determination) and the increase in the chemical reaction rate. This is manifested in the greater slope of the curves of the peaks of the metal-containing ions. The insignificant stabilization of the vapour of $Ir(aa)_3$ and $Rh(aa)_3$ in a reducing atmosphere is known [20]. It follows from an analysis of the temperature curves that in the presence of hydrogen the relative amount of free ligand in the gaseous reaction products increases in the temperature range up to 450°C. The amounts of CO and H_2O also increase at higher temperatures. Hydrogen does not participate quantitatively in the reaction, but the increase in intensity of the ion peak of the free ligand Haa (almost double the molecular ion peak) indirectly testifies to a decrease in the amounts of carbon and oxygen in the solid reaction products.

Oxygen

Study of the thermal decomposition of $Ru(aa)_3$ in the presence of oxygen showed that the vapour of the complex is unstable at the temperature of evaporation (in our case 170°C). This is seen in sharp changes in peak intensities in the mass spectrum at the moment of oxygen entry into the reaction zone. For simplicity, in Fig. 2c this change is shown for only two peaks: those of the molecular ion and the free ligand. Visual control for $Ru(aa)_3$ in the evaporation chamber in the condensed phase after a prolonged experiment did not demonstrate its appreciable decomposition.

Thus, it is possible to ascertain that the thermal stability of $Ru(aa)_3$ vapour decreases in an oxygen atmosphere. A major product of thermolysis in this case throughout the range of temperatures is CO_2, with a significant amount of free ligand Haa up to 300–350°C.

It has been established [6] that the preparation of suitable RuO_2 films is possible by carrying out the decomposition in oxygen. From dependence 1 in Fig. 2c, it follows that, with the use of $Ru(aa)_3$ as precursor under conditions of molecular flow in a mixture with oxygen, a significant proportion of the initial compound will be lost. However, it is also known [21] that the introduction of trifluoromethyl groups into the ligand increases the thermal stability of the metal β-diketonate vapour.

Thermolysis of $Ru(tfa)_3$ vapour

Figure 3 shows the temperature dependence of the ion peaks in the mass spectrum corresponding to the change in composition of the main gaseous products formed on the thermolysis of $Ru(tfa)_3$ vapour in vacuum (a), hydrogen (b) or oxygen (c). These curves reveal that for ruthenium β-diketonates the conclusion concerning the increase in the threshold of thermal stability of the vapour following the introduction of fluoromethyl substituents into the ligand is a fair one. The threshold of stability of $Ru(tfa)_3$ is 260°C higher than that for $Ru(aa)_3$ in vacuum. The threshold temperatures of the investigated ruthenium(III) β-diketonates are listed in Table 3.

Another distinctive feature of the thermal decomposition of $Ru(tfa)_3$ vapour is the absence of free ligand Htfa in the gaseous reaction products. This absence

Table 3 Threshold temperatures of thermolysis of $Ru(aa)_3$ and $Ru(tfa)_3$ vapour

Compound	$Ru(aa)_3$			$Ru(tfa)_3$		
Atmosphere	Vacuum	H_2	O_2	Vacuum	H_2	O_2
$T_{threshold}$ (±10°C)	230	240	<170	490	220	260

can not be explained by the high threshold temperature of decomposition of $Ru(tfa)_3$ vapour and in comparison by the low temperature for the ligand vapour (the vapour of the ligand is reported to be stable up to 340°C [22]). As concerns the significant decrease in the thresholds for $Ru(tfa)_3$ vapour in the presence of oxygen and hydrogen, the free ligand is again absent from among the gaseous reaction products. It is possible to explain this fact if it is considered that the introduction of the strong electron-attracting substituent into the ligand hinders the dehydrogenation of the complex by ligand radicals during thermal decomposition. As a result, we observed only fragments of the ligand Htfa and its oxidation products (Fig. 3c, in oxygen) in the gas-phase composition at the outlet from the reaction zone.

Among the products of decomposition of $Ru(tfa)_3$ vapour, CO, CO_2 and H_2O are accompanied by HF and CF_3, the latter probably as a radical.

Hydrogen

A comparative analysis of the data on the thermal decomposition of $Ru(tfa)_3$ in the presence of hydrogen (Fig. 3b) or in vacuum reveals a decrease in the threshold temperature of the beginning of the process by 270°C. However, no qualitative change occurs in the composition of the gaseous reaction products, which do not contain the free ligand Htfa.

On the other hand, there are quantitative changes in the gas-phase composition: more than double the relative amount of CO, that of HF is also increased, and there is a simultaneous decrease in CO_2. The hydrogen does not participate quantitatively in the reaction, i.e. the intensity of the ion peak $[H_2]^+$ on elevation of the reactor temperature is practically unchanged; more exactly, there is a slight increase at high temperatures (hydrogen is one of the gaseous products of thermolysis).

Oxygen

The process of thermolysis of $Ru(tfa)_3$ vapour in the presence of oxygen is shown in Fig. 3c. It is evident that, as was the case in hydrogen, there is a significant decrease in the threshold temperature. The rate of reaction also increases, and changes occur in the composition of the gaseous reaction products. In this case the major gaseous product is CO_2.

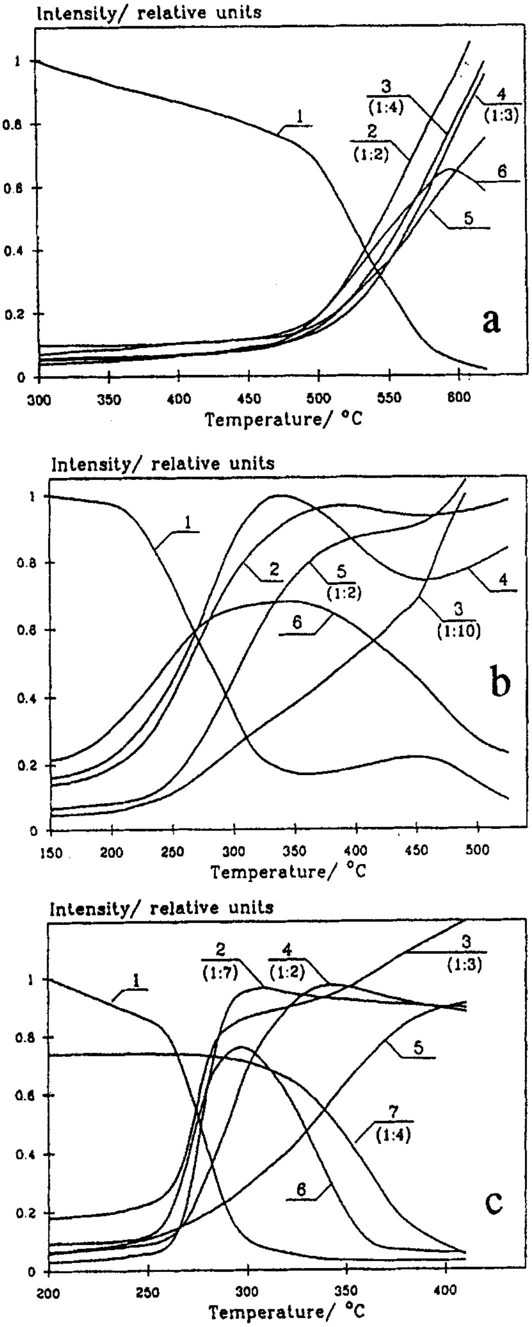

Fig. 3 Temperature dependence of intensities of ion peaks corresponding to the main gaseous products of thermal decomposition of Ru(tfa)$_3$ vapour in vacuum (a), in hydrogen (b) or in oxygen (c): $[Ru(tfa)_3]^+$ (1), $[CO_2]^+$ (2), $[CO]^+$ (3), $[H_2O]^+$ (4), $[HF]^+$ (5), $[CF_3]^+$ (6), $[O_2]^+$ (7)

The feature of the process of thermal decomposition of $Ru(tfa)_3$ vapour in oxygen is that the oxygen concentration does not change in the temperature range up to 300–310°C. The decrease in the stability threshold in this case, as for hydrogen, is probably due to the influence of reactant gas absorbed on the reactor surface on the process of thermolysis.

The intensity of the ion peak corresponding to the radical CF_3 reaches a maximum at 290–330°C, as was the case in hydrogen. Recombination of this species and a simultaneous increase in intensity of the $[HF]^+$ ion peak are then observed.

Kinetic parameters of thermolyses of Ru(aa)₃ and Ru(tfa)₃ vapour

From the temperature curves in Figs 2 and 3, the kinetic parameters of the investigated processes were calculated. In [22], it was shown that with high accuracy the activation curves are of first order with respect to the initial compound. From the balance equation relating to the components of the initial compound in the reaction chamber (molecular flow and irreversibility of vapour thermolysis) for a first-order system, the following empirical formula holds for the effective rate reaction constant:

$$K=\{(A_t+A_e)\times(T/M)^{1/2}\times[(I_{oi}/I_i)\times(T_o/T)^{1/2}-1)\}/V,$$

where A_t and A_e are constant factors in the values of the gas flow conductivity ($F_t=A_t\times(T/M)^{1/2}$) of the tubing connecting the evaporation chamber with the reaction chamber and the effusion outlet of the reactor, respectively (determined from the geometrical sizes); I_{oi} is the intensity of the ion peak of the initial compound measured at any temperature T_o before the threshold of thermal stability; I_i is the current value of the ion peak intensity measured at temperature T; V is the volume of the reaction chamber; and M is the molecular mass of the initial compound.

The calculated temperature dependences of the rate reaction constants of thermolysis of $Ru(aa)_3$ and $Ru(tfa)_3$ vapour in vacuum, oxygen and hydrogen are shown in Fig. 4. The effective values of the parameters in the Arrhenius equation are listed in Table 4. For the thermal decomposition of $Ru(tfa)_3$ in oxygen, use of this equation is possible, for in the temperature range where the calculations of K are carried out the order of reaction with respect to oxygen is close to zero. The order of reaction with respect to hydrogen is close to zero in a wider interval of temperatures for appropriate reactions. For all other cases, the experimental points correspond well to a direct linear temperature dependence of the thermolysis rate constant in appropriate coordinates. However, for the process of thermal decomposition of $Ru(aa)_3$ vapour, it is possible to allocate three regions with various values of parameters. At low temperatures,

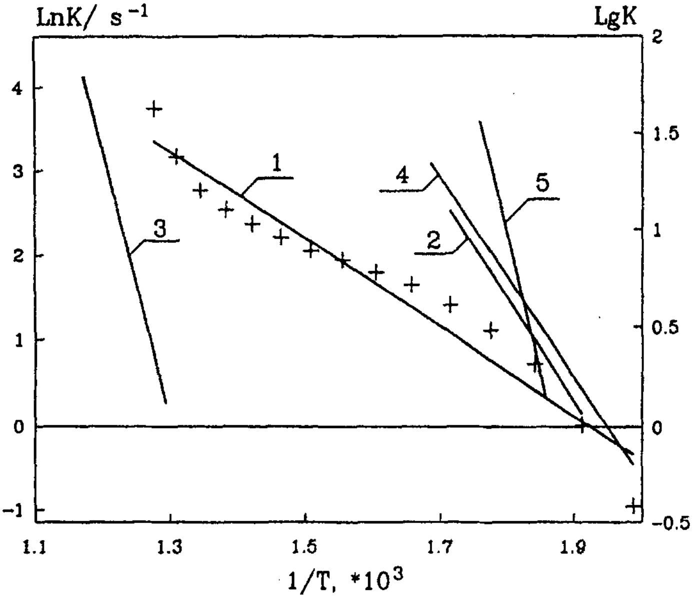

Fig. 4 Dependence of logarithm of rate constant on reciprocal temperature for the thermolysis of $Ru(aa)_3$ vapour in vacuum (1) or in hydrogen (2); and of $Ru(tfa)_3$ in vacuum (3), in hydrogen (4) or in oxygen (5)

Table 4 Effective Arrhenius parameters of thermolysis of $Ru(aa)_3$ and $Ru(tfa)_3$ vapour under various conditions

Compound	$Ru(aa)_3$		$Ru(tfa)_3$		
Atmosphere	Vacuum	H_2	Vacuum	H_2	O_2
E_a/kJ mol^{-1}	43.1±7.5	100.4±4.3	263.8±3.8	97.7±1.5	276.1±4.8
K_o/s^{-1}	$2.17\cdot10^4$	$1.24\cdot10^{10}$	$8.89\cdot10^{17}$	$8.78\cdot10^9$	$8.86\cdot10^{26}$

E_a=81.1±5.2 kJ mol^{-1}, K_o=1.39×10^8 s^{-1}; at intermediate temperatures, E_a=28.2±2.7 kJ mol^{-1}, K_o=1.35×10^3 s^{-1}; and at high temperatures, E_a=115.3±4.5 kJ mol^{-1}, K_o=1.87×10^9 s^{-1}. These regions are explained by the change in the energy of absorption of the initial compound on the surface where the thermal decomposition takes place.

Conclusions

Study of the processes of evaporation and thermal decomposition of $Ru(aa)_3$ and $Ru(tfa)_3$ vapour in a wide temperature range under different conditions demonstrates that they are perspective precursors in CVD processes for the preparation of RuO_2 and Ru films.

The complex Ru(tfa)$_3$ has good characteristics as a precursor, because of the high volatility and thermal stability of its vapour in vacuum and in the presence of oxygen. There are no problems of the transport of the compound to the surface of the substrate, and at the same time there is no need for an appreciable increase of the deposition temperature. Acceptable temperatures for the preparation of RuO$_2$ films by means of the thermal decomposition of Ru(tfa)$_3$ and Ru(aa)$_3$ in oxygen atmosphere are 300°C and higher.

A comparison of the threshold temperatures of thermolysis of Ru(aa)$_3$ and Ru(tfa)$_3$ vapour in vacuum confirms the known conclusions concerning the increase in stability of complexes of metals with β-diketones following the introduction of trifluoromethyl substituents into the ligand. The qualitative difference in the compositions of the gaseous products of thermal decomposition of these compounds merits attention. The free ligand is present in the products of thermolysis of Ru(aa)$_3$, whereas it is totally absent from those of Ru(tfa)$_3$. Similar differences are observed in the mass spectra of these compounds.

One further experimental result deserving attention is the insignificant increase in the threshold of thermal stability of Ru(aa)$_3$ vapour in the presence of hydrogen, and the significant decrease for Ru(tfa)$_3$ vapour under similar conditions. Although this might appear unusual, it is not in contradiction with literature data. An increase in thermal stability is known for iridium and rhodium acetylacetonates [20] and a significant decrease for fluoro-substituted β-diketonates of palladium(II) and platinum(II) [22]. The reason for this phenomenon lies in the features of the electronic structures of the investigated complexes, the contribution of this being determined both by the central metal atom and by the ligand.

A comparison of the temperature curves for Ru(aa)$_3$ and Ru(tfa)$_3$ obtained at various directions and rates of temperature change leads to the assumption that the observable effects stem from the change in catalytic activity on the surface of the reaction zone of the condensed product. In particular, these effects are observed as breaks in the curves of the intensities of the molecular ion peaks in Figs 2a,b and 3b in the temperature range around 450°C, and as changes in the activation parameters of the thermolysis of Ru(aa)$_3$ vapour. In a forthcoming publications, we hope to explain the nature of this phenomenon by means of chemical and phase structure analysis of films formed on thermolysis.

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