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Study of temperature dependencies of saturated vapor pressure of ruthenium(III) beta-diketonate derivatives

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Abstract Complexes of ruthenium(III) with the following beta-diketones: 2,4-pentanedione ($Ru(acac)_3$), 1,1,1-trifluoro-2,4-pentanedione ($Ru(tfac)_3$), 2,2,6,6-tetramethyl-3,5-heptanedione ($Ru(thd)_3$), 2,2,6,6–tetramethyl-4-fluoro-3,5-heptanedione ($Ru(tfhd)_3$) and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione ($Ru(ptac)_3$) were synthesized and identified by means of mass spectrometry. By effusion Knudsen method with mass spectrometric registration of gas phase composition the temperature dependencies of saturated vapor pressure were measured for ruthenium(III) compounds and the thermodynamic characteristics of vaporization processes enthalpy ΔH_{T^*} and entropy ΔS^{o}_{T*} of this complexes were determined.

Keywords Ruthenium(III) · β-Diketonates · Vapor pressure · Thermodynamic characteristics

Introduction

Metal ruthenium and thermodynamically stable ruthenium dioxide RuO_2 possess a number of practically attractive chemical and physical properties. Ruthenium is actively used in heterogeneous and homogeneous catalysis [1, 2], in hydrogenation reactions [3, 4], in Fischer–Tropsch reactions [5]. Thin-film materials based on metal ruthenium are intensively used for the production of electrodes and corrosion-proof diffusion barrier layers for further deposition of tantalum oxide (Ta_2O_5) [6] and barium strontium titanate [$(Ba,Sr)TiO_3$] in gigabit-scale dynamic random access memories (DRAMs) because it has low resistivity, high chemical stability and etching properties [7, 8]. At present, increasing attention is paid to seedless diffusion barrier atomic layer deposition (ALD) applications for the 65 and 45 nm node for subsequent plating of Cu [9–12]. For fabricating Ru-containing thin films, chemical vapor deposition (CVD) and ALD have attracted the most attention because they permit deposition of Ru-containing conformal films on uneven surfaces of different types and is relatively easy to operate [12]. Different classes of the volatile ruthenium-containing compounds are used to deposit ruthenium layers: inorganic compounds (chlorides), carbonyls, cyclopentadienyl derivatives, allyl derivatives, heteroligand complexes, etc. [13]. One of the most attractive classes of volatile ruthenium-containing compounds is the beta-diketonate derivatives due to their high volatility and thermal stability [14, 15]. However, the data on vapor pressure for the majority of volatile ruthenium complexes, including beta-diketonates, are almost absent. Investigation of vaporization of these compounds, determination of the fundamental quantitative thermodynamic data are the relevant problems for further efficient development of technological deposition processes. To this moment, vapor pressure data obtained for vaporization of $Ru(acac)_3$ and $Ru(tfac)_3$ were published by us [16, 17]. The purpose of this work is investigation of vaporization processes in a wide range of ruthenium(III) beta-diketonates and establishment of the effect of end substituents and γ-F substitution on the volatility of the complexes.

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Experimental

Synthesis and identification of Ru compounds

All beta-diketonate derivatives of ruthenium(III) were synthesized according to original procedure developed by us [18], starting from hexafluorocomplexes of ruthenium(V) with following reduction up to Ru^{3+} and interaction of aqua-complexes of Ru^{3+} with beta-diketones at heating and neutralization with KOH up to pH 5–6. 2,2,6,6-Tetramethyl-4-fluoro-3,5-heptanedione has been kindly given by Dr. J. Norman, Air Products Inc., USA. The purification of Ru compounds was made by the method of vacuum zone sublimation at $p = 6$ Pa and temperature range 323–473 K depending on nature of ligand. $Ru(ptac)_3$ was purified by the method of column chromatography on SiO_2, solvent was the mixture of benzol-hexane. The substances were identified by the methods of mass spectrometry. The yield of compounds varied from 50 to 90% (exclusion is $Ru(tfhd)_3$, the yield of which was some percents). Almost all compounds are red crystalline substances, $Ru(ptac)_3$ is a red liquid.

The mass spectra of the gas-phase ruthenium(III) complexes were recorded with a MI-1201 mass spectrometer with the energy of ionizing electrons 35 eV. The source temperature was 373 K for $Ru(acac)_3$, 333 K for $Ru(tfac)_3$, 381 K for $Ru(thd)_3$, 388 K for $Ru(tfhd)_3$, and 363 K for $Ru(ptac)_3$. The limiting resolution of MI-1201 mass spectrometer within the mass number range 1200 a.m.u was not less than 1000 at a level of 10% of the peak height.

Vapor pressure

The temperature dependencies of saturated vapor pressure of the ruthenium(III) complexes were investigated by means of Knudsen's effusion method with mass spectrometric registration of gas phase composition using the equipment described in detail in [19, 20]. Experiments were performed using MI-1201 mass spectrometer mentioned above to analyze the composition of the gas phase. Vapor source was placed directly before the entrance slit of the ionizer—ion source of the mass spectrometer. A cylindrical effusion chamber was made of molybdenum; the dimensions of the internal cavity were: $d = 7$ mm, $h = 8$ mm. Effusive hole was 0.3 mm in diameter; the channel length was 0.2 mm. Weighed portions of 2–3 mg of the compound were vaporized at different temperatures within the required temperature range till complete disappearance of the ion peaks corresponding to the molecular forms of compound vapors. The temperature of effusion chamber was changed stepwise at an arbitrary step. At each established temperature, full mass spectrum was recorded. The temperature of effusion chamber was maintained with the help of PIT-3 PID controller that allowed stabilizing temperature at accuracy of 0.1 K for a long time. To carry out calibration of the mass spectrometer, a published procedure involving evaporation of a known amount of the substance was used [19]. The limiting error of pressure measurement was 10%.

The partial pressure of the vapor in Knudsen chamber was calculated on the basis of the amount of evaporating substance using equation [19]:

$$P_i = \frac{17.14 W \mathrm{I}_i \mathrm{T}_i}{S_{eff} M^{1/2} \sum_i \int_0^t I_i T_i^{1/2} dt},$$

here W is the mass of the substance evaporated during the whole experiments, I_i, T_i is measured intensity under the established temperature mode, $S_{eff} = K_a$ is the product of Klausing coefficient and the area of the effusion orifice, I_i and T_i are the current intensity and temperature during the establishment of isothermal regime. Experimental data are presented as the equation $\lg (p, \text{Torr}) = A - B/(T, \text{K})$, where $A = \Delta S^{\circ}_{T*}/4.575 + 2.88$ и $B = \Delta H_{T*}/4.575$, T^* is mean temperature in the examined interval. For vapor pressure researches the Ru compounds after two times of sublimation in the vacuum were used.

Results and discussion

Synthesis and identification of Ru compounds

The synthesis procedure developed by us for obtaining beta-diketonate derivatives of ruthenium(III) and described in detail in [18] gives the yield of compounds after purification within the range 65–90%.

$$[RuF_6]^- \xrightarrow[\text{reducer}]{\text{Acid medium}} \left[Ru(H_2O)_n\right]^{3-} \xrightarrow[\text{pH control}]{\text{HL,KOH}} RuL_3 \qquad (1)$$

The data on identification of the compounds by means of IR, NMR spectroscopy, and melting point determination, were reported therein, too. When we use reaction (1) to obtain a liquid complex $Ru(ptac)_3$ and apply column chromatography on SiO_2 for subsequent purification, the yield of the product decreases to 50%, which is likely to be connected with partial decomposition of the compound on the column during chromatography process. The $Ru(tfhd)_3$ complex can be obtained according to reaction (1) only with a small yield (several per cent). For clearing up the reason of such low yield additional ^1H NMR study of Htfhd water–ethanol solutions in different mediums was carried out. The research has shown that Htfhd destruction occurs in acid medium. It was confirmed by appearance of additional shifts in ^1H NMR spectra. However, practically 100% enol form of Htfhd solution is observed in alkaline medium. Thus ^{1}H NMR study of Htfhd solutions has shown that the synthesis of Ru(tfhd)$_3$ should be carried out in alkaline conditions. However, the beginning of the formation of ruthenium hydroxide Ru(OH)$_3$ at pH $\geq$ 6 sharply limits pH interval, in which the realization of reaction is possible. This may be one of the reasons of a low yield o the target product. Compounds Ru(tfhd)$_3$ and Ru(ptac)$_3$ were synthesized for the first time.

The mass spectra of all the synthesized beta-diketonate derivatives of ruthenium(III) contain intensive peaks of molecular ions, as well as the peaks corresponding to $[L_2Ru]^+$, where L is a beta-diketonate ligand: Ru(acac)$_3$–$[RuL_3]^+$ (57%), $[L_2Ru]^+$ (100%); Ru(tfac)$_3$–$[RuL_3]^+$ (48%), $[L_2Ru]^+$ (100%); Ru(thd)$_3$–$[RuL_3]^+$ (100%), $[L_2Ru]^+$ (32%); Ru(tfhd)$_3$–$[RuL_3]^+$ (100%), $[L_2Ru]^+$ (10%); Ru(ptac)$_3$–$[RuL_3]^+$ (100%), $[L_2Ru]^+$ (48%). This study showed that all prepared complexes in gas phase are one-phase and one-component compounds of the composition RuL$_3$. Within the investigated temperature range, relative intensities of ion peaks in the mass spectrum do not change, which is an evidence of thermal stability of complex vapors within this temperature range.

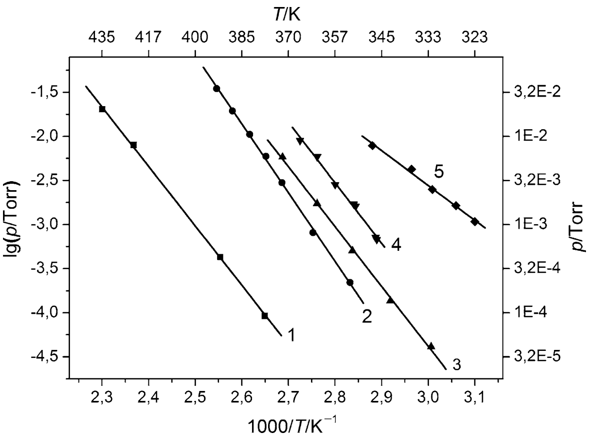

Fig. 1 Dependencies of logarithm of saturated vapor pressure on reciprocal temperature for the complexes Ru(acac)$_3$—**1**, Ru(thd)$_3$—**2**, Ru(tfhd)$_3$—**3**, Ru(tfac)$_3$—**4**, Ru(ptac)$_3$—**5**

Vapor pressure

By present, the main source of the information on the volatility of metal complexes with organic ligands and on the quantitative thermodynamic characteristics of vaporization processes are experimental measurements of saturated vapor pressure. On Fig. 1 the temperature dependencies of saturated vapor pressure of the Ru(III) complexes with beta-diketones studied in this work are presented. Using these dependencies standard thermodynamic characteristics of enthalpy ΔH_{T^*} and entropy $\Delta S^{\circ}_{T^*}$ of sublimation and evaporation were calculated (Table 1).

It was shown in the basis of p–T dependencies that the most volatile compound among the complexes of ruthenium(III) within the investigated temperature ranges is Ru(ptac)$_3$ (Fig. 1). An increase in vapor pressure of metal complexes with c beta-diketones (by several orders of magnitude) when a fluorine-containing substituent is introduced into the chelate molecule was observed previously [21]. A transition from Ru(III) acetylacetonate to Ru(III) trifluoroacetylacetonate (substitution of one –CH$_3$ ground for –CF$_3$) causes an increase in vapor pressure by 2–3 orders of magnitude. Substitution of methyl groups for tert-butyl in the beta-diketonate ligand (compounds Ru(acac)$_3$ and Ru(thd)$_3$) also results in an increase in volatility by 2 orders of magnitude within temperature range 377–393 K (Fig. 1). It should be noted that the introduction of fluorine atom into the γ-position of 2,2,6,6-tetramethyl-3,5-heptanedione has not substantial effect on the volatility of the compound; these two compounds are also close to each other in thermodynamic parameters.

Previously we published the data on the temperature dependence of vapor pressure for Ru(acac)$_3$, measured using the flow method, and for Ru(tfac)$_3$, measured using the static

Table 1 Temperature dependences of the saturated vapor pressure, enthalpy (ΔH_{T^*}) and entropy ($\Delta S^{\circ}_{T^*}$) of evaporation and sublimation of ruthenium(III) complexes, normalized to the mean temperature (T^*) in the examined interval (ΔT)

Compound	Process	ΔT, K	n	lg(p, Torr) $\pm \sigma = A - B/(T, K)$			ΔH_{T^*} (kJ mol^{-1})	$\Delta S^{\circ}_{T^*}$ (J mol^{-1} K^{-1})
				A	B	σ		
Ru(acac)$_3$	Sub.	377–434	4	13.8	6750	0.03	129.1 ± 2.0	210.0 ± 4.9
Ru(thd)$_3$	Sub.	353–393	7	18.4	7790	0.03	149.2 ± 2.2	297.0 ± 6.0
Ru(tfhd)$_3$	Sub.	332–372	5	16.0	6790	0.03	130.0 ± 2.7	251.1 ± 7.5
Ru(tfac)$_3$	Sub.	346–367	7	16.7	6870	0.04	131.4 ± 4.6	265 ± 13
Ru(ptac)$_3$	Evap.	322–347	5	9.3	3960	0.03	75.7 ± 3.3	123.1 ± 9.8

n number of points

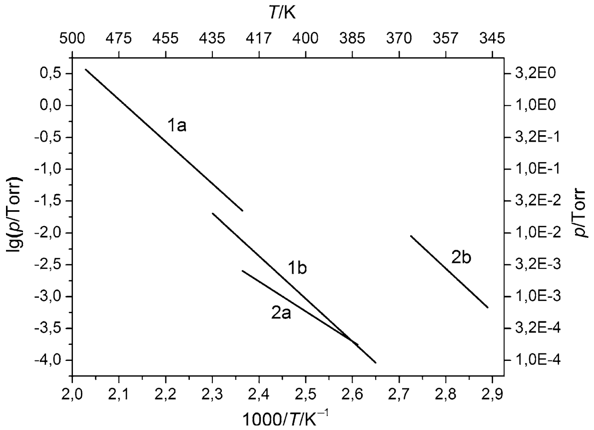

Fig. 2 Dependencies of logarithm of saturated vapor pressure on reciprocal temperature for the complexes Ru(acac)$_3$—**1**, and Ru (tfac)$_3$—**2**, published earlier in [16, 17] (a) and obtained during this work (b)

method with the membrane zero-gauge [16, 17]. Thermodynamic characteristics of sublimation process for Ru (acac)$_3$ ($\Delta H_{T^*} = 127.0 \pm 0.9$ kJ mol^{-1}), $\Delta S^{o}_{T^*} = 212.5 \pm 2.0$ J mol^{-1} K^{-1} [16, 17]) are well agreed with one another for Knudsen and flow methods that proves the assumption about monomolecular structure of vapor of such compounds (Fig. 2).

The difference in the values of thermodynamic parameters obtained for Ru(tfac)$_3$ ($\Delta H_{T^*} = 90.0 \pm 3.0$ kJ mol^{-1}), $\Delta S^{o}_{T^*} = 163.2 \pm 7.2$ J mol^{-1} K^{-1} [16, 17]) using different methods is likely to be explained by different ratios of the isomers in the mixture under investigation. Previously, the product after synthesis and double sublimation in vacuum was investigated. According to the data published in [22], in this case a mixture of two isomers, *cis*- and *trans*-, is formed in the solid phase; the melting point of the cis-form is 403 K, and the melting point of the trans-form is 443 K. So, within the temperature range of sublimation process study 383–423 K in our work [16, 17], the effects caused by *cis*-isomer melting are superimposed, which affects the final calculated enthalpy and entropy of the process. A detailed investigation of vapor pressure for pure forms of *cis*- and *trans*-isomers of Ru(tfac)$_3$ will be published by us in the nearest future.

The following row of volatility was obtained for beta-diketonaet derivatives of ruthenium(III) on the basis of the measured p–T dependencies (for $p = 10^{-3}$ Torr): Ru (ptac)$_3$ (322 K) > Ru(tfac)$_3$ (348 K) > Ru(tfhd)$_3$ (357 K) > Ru(thd)$_3$ (364 K) > Ru(acac)$_3$ (402 K). These data are in agreement with the qualitative volatility rows of ruthenium(III) beta-diketonates arranged on the basis of the TG data published by us previously [18]. It was shown that variation of ligands in the investigated ruthenium(III) complexes can change vapor pressure at the same temperature by several orders of magnitude.

Conclusions

Thus, by effusion Knudsen method with mass spectrometric registration of gas phase composition the temperature dependencies of saturated vapor pressure were measured for five ruthenium(III) compounds, the thermodynamic characteristics of vaporization processes ΔH_{T^*} and $\Delta S^{o}_{T^*}$ of this complexes were calculated. A comparison of volatility between the complexes inside the class of beta-diketonate derivatives was carried out; the effect of the end substituents and γ-F substitution on the volatility of the complexes was established.

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