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Thermodynamic characteristics of phase conversion of structural isomers for volatile complex of ruthenium (III) trifluoroacetylacetonate

S. V. Sysoev · T. N. Cheremisina · L. N. Zelenina · S. V. Tkachev · K. V. Zherikova · N. B. Morozova · N. V. Kuratieva

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Abstract The comprehensive analysis of volatile β-diketonate compound—ruthenium(III) trifruoroacetylacetonate ($Ru(tfac)_3$)—was carried out. By means of flow method in quasi-equilibrium conditions and static method the temperature dependencies of saturated vapor pressure have been measured over solid and liquid *cis*- and *trans*-modifications of $Ru(tfac)_3$ and isomer mixture. The thermodynamic characteristics of sublimation, evaporation, melting, and phase conversion have been calculated for structural isomers. Also by differential-scanning calorimetry the temperature meanings and the thermodynamic characteristics of melting have been determined for individual isomers of $Ru(tfac)_3$ and their mixtures. By XRD the structures for *cis*- and *trans*-modifications have been determined. Both structures consist of neutral molecules arranged in pseudo layers.

Keywords Vapor pressure measurements · Thermodynamic characteristics · Structural parameters

Introduction

The volatile coordination compounds including metal β-diketonates are perspective precursors for obtaining of metal and oxide functional layers by chemical vapor deposition. Quantitative physical–chemical characteristics, data on saturated vapor pressure and thermal stability of these compounds are necessary to choose optimal conditions for carrying out such processes. These data substantially depend on ligand structure. It is known that the introduction of fluoro-containing groups into the ligand substantially increases the volatility and thermal stability of such compounds [1]. The structural isomerism occurring among complexes with asymmetrical ligands also influences on their physico-chemical properties (vapor pressure, melting point, storage, and use stability). The aim of current investigation is to show the influence of this fact by example of ruthenium(III) trifluoroacetylacetonate, $Ru(tfac)_3$, the one of perspective precursor for obtaining thin-film structures with RuO_2.

Early, we measured the temperature dependencies of saturated vapor pressure of the mixture *cis*- and *trans*-modifications $Ru(tfac)_3$ by the static method with a silica-membrane zero gauge [2] and by effusion Knudsen method with mass spectrometric registration [3]. The thermolysis of $Ru(tfac)_3$ was investigated too [2]. Melting temperatures of *cis*-modification (132–133 °C) and *trans*-modification (172.5–173.5 °C) are represented in [4].

Experimental

The synthesis of $Ru(tfac)_3$ was carried out according to procedure for obtaining β-diketonates of platinum metals developed by us [5]. The product was purified by zone sublimation in vacuum gradient furnace. The yield of compound after purification was within the range 75–90%. As a result of synthesis the mixture of isomers was obtained with prevalence of *trans*-form (on average about 80% *trans*-$Ru(tfac)_3$).

S. V. Sysoev (✉) · L. N. Zelenina · S. V. Tkachev ·
K. V. Zherikova · N. B. Morozova · N. V. Kuratieva
Nikolaev Institute of Inorganic Chemistry SB RAS, Lavrentiev
ave., 3, 630090 Novosibirsk, Russia
e-mail: tv@niic.nsk.ru

T. N. Cheremisina
Novosibirsk State University of Architecture and Civil
Engineering, Novosibirsk, Russia

The compound was identified with NMR for obtaining quantitative data about isomer containing. The ^{19}F NMR spectra of complexes were recorded with MSL 300 (BRUKER). The chemical shifts were determined relatively to fluorine signal in trifluoroacetic acid and then were reevaluated relatively to free F_2.

The structures for *cis*- and *trans*-Ru(tfac)$_3$ have been determined at 150 K by XRD. Crystallographic data for *cis*-$C_{15}H_{12}F_9O_6Ru$: $a = 8.6562(3)$, $b = 12.6941(3)$, $c = 17.8776(5)$ Å, $\beta = 93.129(1)°$, sp. gr. $P2_1/n$, $V = 1961.51(10)$ Å^3, $Z = 4$, $d_{\mathrm{calc}} = 1.897$ g/mL, $R = 0.0565$; for *trans*-$C_{15}H_{12}F_9O_6Ru$: $a = 13.4060(3)$, $b = 14.5946(3)$, $c = 20.1316(4)$ Å, sp. gr. $Pcab$, $V = 3938.85(14)$ Å^3, $Z = 8$, $d_{\mathrm{calc}} = 1.890$ g/mL, $R = 0.0840$. Both structures consist of neutral molecules. Metal atom coordinates six oxygen atoms of three β-diketonate ligands. Distance Ru–O in *cis*-Ru(tfac)$_3$ is about 1.99–2.03 Å, in *trans*-Ru(tfac)$_3$—1.99–2.02 Å.

In spite of both structures consist of neutral molecules it should be noted, that according to distribution of structural units and their relative orientation, they seemed to be pseudo layers. Distances Ru…Ru in the molecules, hexagonally coordinated inside layers, are established to be about 7.6014(3), 7.6374(3) и 8.6562(3) Å for *cis*-Ru(tfac)$_3$ and 7.326, 7.577 и 7.715 Å for *trans*-Ru(tfac)$_3$. There is more detailed information about experiments and crystal structures in [6].

Calorimetric measurements were carried out with scanning calorimeter Setaram DSC 111 at a heating rate of 1–3 K/min and a sample mass of 20–30 mg. Under the conditions applied, the compound samples were in vacuum glass containers. The errors in the heat effect measurements were less than 2% from determined value. The samples exhibited only fixed phase transition (melting) over the temperature range studied (300–473 K).

During the measurements, the investigated substance was contained in evacuated glass ampoule.

The density of saturated vapor above Ru(tfac)$_3$ was measured with a flow method in atmosphere of a dry inert gas carrier (helium) [2, 7]. The amount of substance vaporized on the passage of certain volume of helium with following condensation in a cold zone was determined by weighing. The total error of this method was not above ±5% with accuracy in the maintenance of temperature ±0.5 °C and the error in the measurement of flow rate ±2%. Measurements were carried out in quasi-equilibrium conditions. The independence of vapor pressure on the helium flow rate was the experimental evidence of this statement. The using of a flow method to study this class of compounds is very useful because of obtaining reliable data with values of vapor pressure being relatively low against a background of partial thermal decomposition. The pressure of saturated vapor was calculated using:

$$P = P_{\mathrm{total}} \frac{n}{n + N}$$

where n is the number of moles of carried compound, N is the number of moles of gas carrier, and P_{total} is total pressure in a system.

The calculation is based on the assumption that the substance vaporizes in the monomolecular form. This fact is sustained by good coincidence of results obtained both by means of flow and static method. Mention should be made of the results obtained both on the loss in mass of the substance and the rise in mass of condensed substance in the cold zone, practically coincided. This indicated that the complex possessed of thermal stability within the studied temperature range.

The separation of isomers was conducted by sublimation carrying over (*trans*-modification) and by liquid chromatography with mixture of benzene and hexane (*cis*- modification) [4].

Results and discussion

Physico-chemical properties (vapor pressure, m.p., thermal stability) of investigated compounds depend on following major factors:

1. The nature of end substituents in chelate ligand;
2. The nature of central metal, forming comflex;
3. The presence of structural isomers.

The introduction of trifluoromethyl end substituents substantially, by orders, increases the volatility of β-diketonates. At the same time, the influence of the nature of

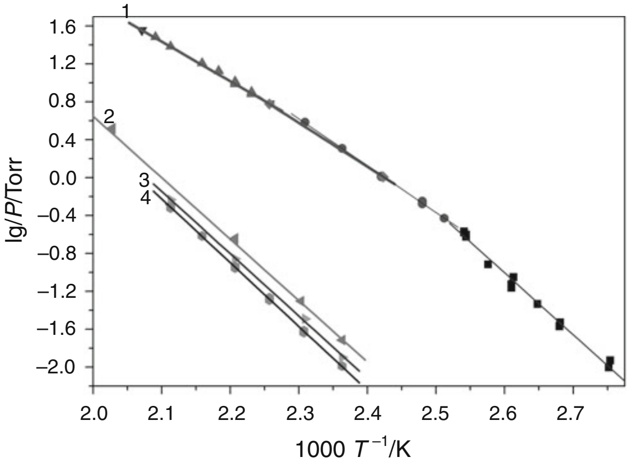

Fig. 1 The temperature dependencies of saturated vapor pressure under β-diketonates of precious metals: (1) solid and liquid Ru(tfac)$_3$(*cis* + *trans*), static and flow methods; (2) solid Ru(acac)$_3$, flow method; (3) solid Rh(acac)$_3$, flow method; (4) solid Ir(acac)$_3$, flow method

Table 1 Thermodynamic characteristics of sublimation and vaporization processes for β-diketonates of precious metals

	Process (method)	Interval T/K	$\Delta H(T)$/kJ mol^{-1}	$\Delta S°(T)$/J K^{-1} mol^{-1}
$Ru(tfac)_3$(*cis* + *trans*)	vap.(static)	443–483	78.1 ± 0.5	136 ± 1
$Ru(tfac)_3$(*cis* + *trans*)	vap.(flow)	448–478	80.3 ± 2	141 ± 4
$Ru(tfac)_3$(*cis* + *trans*)	sub.(flow)	363–393	117.0 ± 2	232 ± 6
$Ru(acac)_3$	sub.(flow)	423–493	127.0 ± 1	212.5 ± 2
$Rh(acac)_3$	sub.(flow)	423–473	128.3 ± 1	211.5 ± 2.5
$Ir(acac)_3$	sub.(flow)	423–473	129.3 ± 1	219.2 ± 2

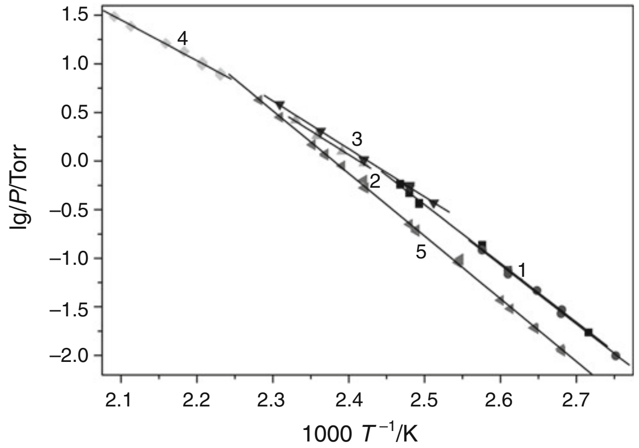

Fig. 2 The temperature dependencies of saturated vapor pressure under solid and liquid *cis*- and *trans*-isomers of $Ru(tfac)_3$: (1) $(cis)_{solid}$; (2) $(cis)_{liquid}$; (3) $(cis + trans)_{liquid}$; (4) $(trans)_{liquid}$; (5) $(trans)_{solid}$

metal atom in complexes of platinum metal including Pt(II) and Pd(II) compounds [8] is not so substantial. The temperature dependences of equilibrium vapor pressure under mixture of *cis*- and *trans*-isomers of $Ru(tfac)_3$ (asymmetrical end substituents $–CF_3$ and $–CH_3$), acetylacetonates $Ru(acac)_3$, $Rh(acac)_3$, $Ir(acac)_3$ (symmetrical end substituents $–CH_3$ and $–CH_3$) obtained by using flow method confirm this fact. The results were shown in Fig. 1. The thermodynamic characteristics of vaporization processes for pointed compounds are listed in Table 1.

In case of different end substituents in ligand the structural isomers are possible; their properties are substantially different.

The temperature dependence of saturated vapor pressure over solid and liquid *cis*- and *trans*-modifications of $Ru(tfac)_3$ and under mixture of isomers, obtained by flow method is shown in Fig. 2. It is obvious, that *cis*- form has considerably higher vapor pressure and lower melting temperature. The vapor pressure, measured over individual solid *cis*-$Ru(tfac)_3$, coincided with values of vapor pressure calculated as difference between vapor pressure under mixture of isomers and that one over trans-modification. Temperature dependencies of vapor pressure over individual liquid *cis*- and *trans*-modifications (the flow method) and liquid mixture of isomers (the static method) are close.

The experimental data developed under the special method are presented in the form $\ln P = A - B/T$. The obtained temperature dependence of the saturated vapor pressure for the investigated complexes and thermodynamic characteristics of the vaporization $\Delta H(T)$ and $\Delta S°(T)$ calculated for mean temperatures of investigated intervals are listed in Table 2.

Also by differential-scanning calorimetry (DSC) melting points and the thermodynamic characteristics of melting were determined for individual isomers of $Ru(tfac)_3$ and their mixtures. Results are listed in Table 3. The data calculated from tensimetric experiments are listed in Table 3 too. Some difference between DSC results and tensimetric data appeared because of neglecting the changes in heat capacities.

The isomer mixture was established to form eutectic, melting at (120 ± 2) °C. *Trans*–$Ru(tfac)_3$ is more thermodynamically stable. The conversion of *cis*-$Ru(tfac)_3$ to

Table 2 The temperature dependencies of saturated vapor pressure and thermodynamic characteristics of sublimation and vaporization of $Ru(tfac)_3$

Compound	$\ln (P/\text{Torr}) = A - B/T$		$\Delta H\ (T)$/kJ mol^{-1}	$\Delta S\ (T)$/J K^{-1} mol^{-1}	Interval T/K	Point numb.
	A	B				
cis-$Ru(tfac)_3$ (sol.)	27.52	14,076	1 17 ± 2	229 ± 4	363–405	15
cis-$Ru(tfac)_3$ (liq.)	20.41	11,202	93 ± 4	170 ± 11	413–429	4
trans-$Ru(tfac)_3$(sol.)	28.78	14,885	123.8 ± 0.4	239 ± 1	373–438	20
trans-$Ru(tfac)_3$(liq)	16.99	9,656	80 ± 2	141 ± 4	448–478	9

Table 3 Thermodynamic characteristics of melting Ru(tfac)$_3$

Compound	Method	T_{melt}/K	$\Delta H(T)_{melt}$/kJ mol^{-1}	$\Delta S°(T)_{melt}$/J mol^{-1} K^{-1}
trans-Ru(tfac)$_3$	DSC	447.8 ± 0.5	35 ± 1	78 ± 2
trans-Ru(tfac)$_3$	Tensim	443.7 ± 3	43 ± 5	98 ± 10
cis-Ru(tfac)$_3$	DSC	408.2 ± 1	17 ± 2	40 ± 2
cis-Ru(tfac)$_3$	Tensim	405.2 ± 3	24 ± 8	60 ± 20
(*trans* + *cis*) eutectic	DSC	392.2 ± 1	24.5 ± 1	63 ± 2
(*trans* + *cis*) eutectic	Tensim	394.2 ± 3	24 ± 5	70 ± 10

trans-Ru(tfac)$_3$ is known to be even at room temperature. Individual *cis*-Ru(tfac)$_3$ converts into isomer mixture, containing 80% of *cis*- and 20% of *trans*-Ru(tfac)$_3$.

Conclusions

Thus, by means of flow method in quasi-equilibrium conditions and static method the temperature dependencies of saturated vapor pressure have been measured over solid and liquid *cis*- and *trans*-modifications of Ru(tfac)$_3$ and isomer mixture. The thermodynamic characteristics of sublimation, evaporation, melting, and phase conversion for structural isomers have been calculated. Also by differential-scanning calorimetry the temperature meanings and the thermodynamic characteristics of melting have been determined for individual isomers of Ru(tfac)$_3$ and their mixtures. The physico-chemical properties for structural isomers are substantially different. The complex set data, reported in the present study, allow giving recommendations concerning optimization of the processes involving the deposition of coatings based on platinum metal beta-diketonates.

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