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PHYSICAL METHODS OF INVESTIGATION

Volatility and Thermal Stability of Vanadyl β-Diketonate Complexes

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Abstract—Thermal behavior and thermodynamic characteristics of vanadyl β-diketonates—acetylacetonate $VO(acac)_2$, dipivaloylmethanate $VO(thd)_2$, and tris-hexafluoroacetylacetonate $VO(hfa)_2$ (Hacac, 2,4-pentanedione; Hthd, 2,2,6,6-tetramethyl-3,5-heptanedione; Hhfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione)—have been studied by thermal analysis and the Knudsen effusion mass spectrometry study of gas phase composition. The compounds have been shown to undergo congruent sublimation. Saturated vapor over the complexes has been shown to comprise monomeric VOL_2 molecules. Absolute values of partial pressures and sublimation enthalpies of these compounds have been determined.

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Vanadium dioxide attracts particular attention among numerous oxide materials showing metal–dielectric (MD) transition. In spite of simple cationic composition, VO_2 shows a number of interesting features: MD transition proceeds instantly ($\tau < 1$ ps) at temperatures close to ambient temperature (68°C for bulk samples) and with giant change in conductivity ($\sim 10^5$ times for single crystals [1]). Electronic transition in vanadium dioxide is accompanied by change in magnetic and optical (in the IR region) properties. It can be caused not only by thermal impact but also under the action of other physical factors (exposure to electric or magnetic field [2], laser radiation [3]). The set of such unique properties makes vanadium dioxide promising key component for a number of new micro devices: electronic switches [4], thermal, optical, and magnetic sensors, metamaterials, memory devices [5–7]. Vanadium dioxide films are obtained by high-vacuum gas-phase methods with different methods of ceramic or metallic target evaporation (laser, ion, or electron beam) [8, 9]. However, expensive high-vacuum equipment makes these methods suitable for preparing laboratory samples only.

In recent time, vanadium dioxide films are prepared by MOCVD method, which is widely used in industry and free from many drawbacks described above. Different modifications of this method are developed (under low [10] and atmospheric pressure [11], with liquid sputtering [12]). Special attention is attracted by the variation of chemical gas-phase deposition using as precursors vanadyl β-diketonates of general formula VOL_2, where L is thd [13], acac [14, 15], and hfa [16, 17]. However, in spite of growing popularity of chemical gas-phase methods for vanadium dioxide films preparation by decomposition of vanadyl β-diketonates, the volatility and thermal stability of the complexes are not studied.

The aim of this work is to study gas phase composition by mass spectrometry, determine thermodynamic characteristics of evaporation processes, and to compare volatility of vanadyl β-diketonates of general formula VOL_2 [L = acac (Hacac, 2,4-pentanedione); thd (Hthd, 2,2,6,6-tetramethyl-3,5-heptanedione); hfa (Hhfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione).

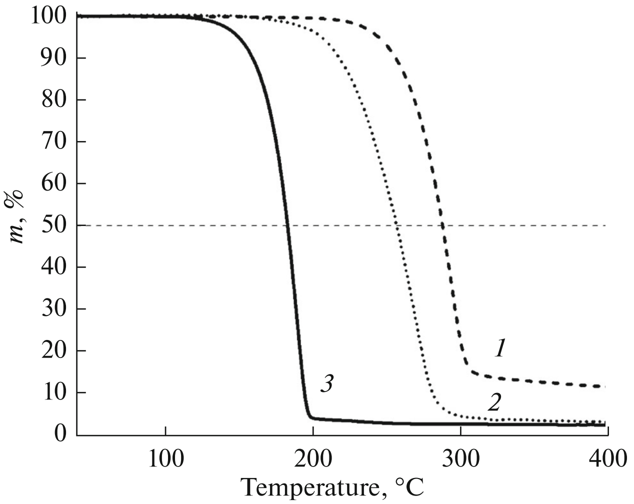
EXPERIMENTAL

Synthesis of $VO(acac)_2$. An aqueous solution (300 mL) of $VOSO_4 \cdot 3H_2O$ (12.3 g) was added dropwise with stirring to an aqueous solution (200 mL) of a mixture of Hacac (15.09 g) and NaOH (6.04 g). The resultant turquoise precipitate was washed with water, dried in air, and sublimed at 190°C and 0.01 mmHg. The identity of the prepared product (265 g/mol) to composition $VC_{10}H_{14}O_5$ was confirmed by the data of elemental analysis and IR spectroscopy.

Found (%): C, 45.43; H, 5.39. Calculated (%): C, 45.30; H, 5.32.

Characteristic bands in IR spectrum (ν, cm^{-1}): 993 ν(V=O); 685 ν(V–O); 1547 ν(C=O); 1520 ν(C=C); 2900–3025 ν(C–H).

Synthesis of $VO(thd)_2$. The synthesis was conducted in aqueous alcohol medium (1 : 1). A solution of $VOSO_4 \cdot 3H_2O$ (8.66 g, 99%) in 100 mL of H_2O was added dropwise to 400 mL of solution of a mixture of 3.05 g NaOH (99%) and 14.03 g of Hthd (Dalchim, 98%) with constant stirring. After 5 h, the resultant



Weight loss curves for complexes VOL_2, where L = acac (*1*), thd (*2*), hfa (*3*).

green product was separated by filtration, washed with water, and dried in air. The compound was purified by sublimation at 0.01 mmHg and 140°C. The identity of the prepared product (433 g/mol) to composition $VC_{22}H_{38}O_5$ was confirmed by the data of elemental analysis and IR spectroscopy.

Found, %: C, 61.08; H, 8.67. Calculated, %: C, 60.96; H, 8.84.

Characteristic bands in IR spectrum (ν, cm^{-1}): 1004 ν(V=O); 2860–3005 ν(C–H); 1540 ν(C=O); 1505 ν(C=C); 1300–1400 and 1430–1600 ν(C–O).

Synthesis of $VO(hfa)_2$. The complex was obtained by dropwise addition of 2 mL of Hhfa (P&M Invest, 98%) to a suspension of a mixture of $VO(SO_4) \cdot 3H_2O$ (1.52 g) and KOH (0.78 g) in acetonitrile (200 mL) with constant stirring. The resultant mixture was placed into a closed flask and stirred for 20 h at ambient temperature. The prepared dark solution was filtered and dried with air flow to give dark green fine-crystalline precipitate. The product was purified by sublimation at 120°C and 0.01 mmHg. The composition $VO(hfa)_2$ was identified by the data of IR spectroscopy.

Characteristic bands in IR spectrum of $VO(hfa)_2$ (ν, cm^{-1}): 941 ν(V=O); 1139–1210 $\nu(CF_3)$; 1620–1644 ν(C=O); 1520–1570 ν(C=C); 2906 ν(C–H).

It should be noted that the product gradually hydrolyses to form vanadyl *tris*(hexafluoroacetylacetonate) monohydrate $VO(hfa)_2 \cdot H_2O$, which is confirmed by the emergence in IR spectrum of characteristic absorption band ν(O–H) at 3320–3700 cm^{-1}.

IR spectra were recorded on a PE-FTIR-1600 spectrometer in the range 400–4000 cm^{-1}, the samples were suspended in Nujol and hexachlorobutadiene.

Thermal analysis was performed on a Sinku-Riko TGA-7000 thermal analyzer (Japan) under an argon atmosphere (heating rate 10 K/min, sample weight 5–9 mg).

The vaporization process of vanadyl β-diketonates was studied by Knudsen effusion mass spectrometry of evaporation products on a MC 1301 instrument. Standard molybdenum effusion cells with evaporation area to effusion area ratio ≥600 were used in the work. Temperature was measured with a Pt-Pt/Rh thermocouple and maintained constant with accuracy ±2°.

RESULTS AND DISCUSSION

Vanadyl β-diketonates were studied by mass spectrometry and thermal analysis.

Figure shows weight loss curves for $VO(acac)_2$, $VO(thd)_2$, and $VO(hfa)_2$, obtained by heating the compounds under atmospheric pressure of argon. In temperature range 35–400°C, the complexes are completely evaporated. Total weight loss is 95% for $VO(hfa)_2$, 94% for $VO(thd)_2$, and 90% for $VO(acac)_2$. A marked amount of residue upon evaporation of vanadyl acetylacetonate can be explained by pyrolysis side reaction at temperature about 300°C. The character of obtained curves of weight loss allows us to suppose congruent evaporation of the complexes. The comparison of temperatures for 50% weight loss leads to the following order of volatility for these compounds: $VO(acac)_2$ (289°C) < $VO(thd)_2$ (257°C) < $VO(hfa)_2$ (183°C).

Vaporization of complexes $VO(acac)_2$, $VO(thd)_2$, and $VO(hfa)_2$ was studied in temperature ranges 340–410, 323–388, and 313–343 K, respectively. Table 1 shows the intensities of the main ions (given for isotope V^{51}) detected in the mass spectra of saturated vapors. Mass spectral analysis provided a possibility to draw a conclusion that monomeric molecules of general formula VOL_2 are present in gas phase over the compounds.

To determine the character of vaporization and quantitative composition of gas phase, we performed experiments on complete isothermal evaporation of weighed samples of VOL_2 complexes [18]. The measurements showed that intensity of ion current (value proportional to partial pressure) remains constant during sublimation of all compounds until complete evaporation of samples, no nonvolatile residues remained in effusion cells after experiment completion. The obtained data indicate that evaporation of vanadyl β-diketonates in the studied temperature range proceeds in congruent mode without marked thermal decomposition by reaction

$$[VOL_2](s) = [VOL_2](g) \text{ (L = acac, thd, hfa).}$$

The results of experiments on complete isothermal evaporation allowed us to calculate by Hertz–Knud-

Table 1. Mass spectra of gas phase over VOL_2 complexes ($U_{\text{ioniz}} = 68$ V)

$VO(acac)_2$ (388 K)		$VO(thd)_2$ (377 K)		$VO(hfa)_2$ (330 K)	
Ion	*I*, %	Ion	*I*, %	Ion	*I*, %
$[VO]^+$	11	$[VO]^+$	15	$[VO]^+$	13
$[(VO)OOC]^+$	43	$[VOCO]^+$	13	$[(VO)(hfa)\text{-}2F]^+$	85
$VO(acac)]^+$	115	$[VO(thd)]^+$	49	$VO(hfa)^+$	54
$[[VO(acac)\text{-}OOCH_2]^+$	35	$[VO(thd)\text{-}3CH_3]^+$	9	$[VO(hfa)F]^+$	244
$[VO(acac)_2\text{-}CH_3]^+$	34	$[VO(thd)_2]^+\text{-}CH_3]^+$	40	$[VO(hfa)_2\text{-}CF_3]^+$	51
$[VO(acac)_2\text{-}3CH_3]^+$	19	$[VO(thd)\text{-}2(CH_3)_3]^+$	7	$[VO(hfa)_2\text{ -}F]^+$	24
$[VO(acac)_2]^+$	100	$[VO(thd)_2]^+$	100	$[VO(hfa)_2]^+$	100

sen equation the absolute values of saturated vapor pressures for the complexes (Table 2).

To determine sublimation enthalpy of the compounds, we studied temperature dependences of ion currents for $I^+_{VOL_2}$, I^+_{VOL}, $I^+_{[VO(thd)-CH_3]}$, $I^+_{[VO(hfa)F]}$. Sublimation enthalpies were calculated by the Clausius–Clapeyron equation using least-squares method from six independent experiments. Taking into account low temperatures of experiments, it was taken in the first approximation that the found values correspond to the standard sublimation enthalpies of complexes. The given errors represent root mean square error for arithmetic mean value of a number of measurements. Recommended data are summarized in Table 2.

The results of mass spectral study of vanadyl β-diketonates evaporation processes show that the complexes are thermally stable and have stable thermodynamic properties in the range 313–410 K. The absolute values of saturated vapor pressure increase in the series $VO(hfa)_2 > VO(thd)_2 > VO(acac)_2$, which agrees well with the data of thermogravimetric measurements. At the same time, the revealed order of volatility of the studied compounds corresponds to the well-known literature data on the effect of ligand nature on variation in volatility of metal β-diketonates [19, 20]. It should be also noted that monomolecular composition of gas phase over $VO(acac)_2$, $VO(hfa)_2$, and $VO(thd)_2$ as well as enhanced volatility indeed provide a possibility to control both composition and thickness of vanadium dioxide films prepared by MOCVD.

Table 2. Absolute values of pressure and sublimation enthalpy for vanadyl β-diketonates

Compound	*T*, K	*P*, Pa	Δ*T*, K	$\Delta_S H^0$(298 K), kJ/mol
$VO(acac)_2$	369	2.1×10^{-1}	340–410	132.3 ± 4.3
$VO(thd)_2$	369	2.7×10^{-1}	325–388	126.5 ± 10.5
	330	4.7×10^{-3}		
$VO(hfa)_2$	330	1.8×10^{-1}	313–343	118.7 ± 9.6

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