

STUDY OF TEMPERATURE DEPENDENCE OF SATURATED VAPOUR PRESSURE OF ZIRCONIUM(IV) β -DIKETONATES

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Abstract

By means of a tensiometric flow method and a static method with a silica-membrane zero gauge, the dependences of saturated vapour pressure on temperature were obtained for the complexes of zirconium(IV) with acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, dipivaloylmethane and pivaloyltrifluoroacetone. The thermodynamic characteristics of the evaporation and sublimation of these complexes were determined.

Keywords: complexes, zirconium(IV) β -diketonates

Introduction

Study of the processes of evaporation and sublimation of Zr(IV) β -diketonates with high volatility and thermal stability in a wide range of temperatures is currently of great interest. These compounds can be used in CVD processes to prepare various types of films and coatings based on zirconium. The tasks of separation and purification requiring the transition of a metal compound from the solid state to the vapour phase can also be successfully solved.

At present, the saturated vapour pressure data have been published [1, 2] only for the complexes of Zr(IV) with acetylacetone (Haa) and dipivaloylmethane (Hdpm). The purpose of the present work is to extend the number of investigated complexes, to determine the influence of ligand substituents on complex volatility and to verify the earlier-obtained data.

The present work is a continuation of thermoanalytical research on complexes of Zr(IV) with β -diketones. We earlier investigated these complexes by DTA in an atmosphere of helium or oxygen or in vacuum. The thermoanalytical data obtained in vacuum revealed a qualitative range of volatility of Zr(IV) β -diketonates. This range is typical for this class of compounds. We also set out to collect quantitative data on this class of compounds.

Experimental

Synthesis

The complexes of Zr(IV) with β -diketones were obtained by the method described in detail in [3]. It consists in the direct interaction of aqueous ethanol solutions of $ZrCl_4$ with β -diketones under heating with the subsequent addition of KOH up to pH 5–6. The complex with hexafluoroacetylacetone, $Zr(hfa)_4$, was prepared under heating with reverse cooling of anhydrous $ZrCl_4$ with a 5-fold excess of Hhfa. The compounds obtained were purified twice by zone sublimation in a vacuum gradient furnace. The substances were identified by IR spectroscopy, chemical analyses for C, H and F and melting point determination. The chemical analysis results and melting points obtained on a Kofler hot stage are presented in Table 1.

Table 1 Results of chemical analysis of Zr(IV) β -diketones

Compound	Content (calc./found)/%			$T_{melt.}/^{\circ}C$
	C	H	F	
$Zr(aa)_4$	49.28/48.39	5.75/5.72	–	194
$Zr(tfa)_4$	34.14/34.72	2.28/2.31	32.43/32.37	130
$Zr(hfa)_4$	26.12/25.89	0.44/0.41	49.62/47.99	39
$Zr(pta)_4$	44.09/43.68	4.59/4.57	26.18/26.05	182
$Zr(dpm)_4$	64.16/63.77	9.23/9.21	–	–

Vapour pressure

The densities of the saturated vapour above $Zr(aa)_4$ and the complexes of trifluoroacetylacetone, $Zr(tfa)_4$, and of pivaloyltrifluoroacetone, $Zr(pta)_4$, were measured by a flow method. The experimental technique was described in detail in [4]. A measured volume of a dry inert gas carrier (helium) was passed through a volume source (4 cm long and 1.5 cm in diameter) filled with the substance under investigation. The precision of temperature maintenance was $\pm 0.5^{\circ}C$, and the error of flow rate measurements was $\pm 1\%$. The amount of substance vaporized on passage of a certain volume of helium was determined by weighing (the loss in mass of the substance in the source and the rise in mass of the substance in the cold zone). The two results practically coincided for the evaporation and sublimation of $Zr(pta)_4$ and the sublimation of $Zr(tfa)_4$, i.e. the substances were not decomposition in the investigated temperature range. Partial decomposition was observed for the evaporation of $Zr(tfa)_4$ and especially for the sublimation of $Zr(aa)_4$. In the latter case, the vapour density values cal-

Table 2 Thermodynamic parameters of vaporization processes of zirconium(IV) β -diketonates

Compound	Process	Number of points	$T_{\text{range}}/^\circ\text{C}$	$\ln P_{(\text{bar})} \pm \sigma = B - A/T$		$\Delta H_{\text{v}}^\circ / \text{kJ mol}^{-1}$	$\Delta S_{\text{v}}^\circ / \text{J (mol K)}^{-1}$	
				B	A			
Silica-membrane zero gauge:								
Zr(hfa) ₄	vap	21	93-183	11.37	5843	$4876/T^2 - 23/T + 0.03$	48.6 ± 0.6	94.5 ± 1.3
Zr(dpm) ₄	vap	18	206-263	9.57	7664	$105427/T^2 - 392/T + 0.37$	63.7 ± 2.7	79.6 ± 5.2
Zr(pta) ₄	vap	16	174-249	16.23	9804	$14968/T^2 - 59/T + 0.06$	81.5 ± 1.0	134.9 ± 2.2
Flow method:								
Zr(pta) ₄	sub	10	115-150	30.88	16230	$39100/T^2 - 190/T + 0.23$	134.9 ± 1.6	256.7 ± 4.1
Zr(pta) ₄	vap	16	180-220	16.13	9864	$71925/T^2 - 303/T + 0.32$	82.0 ± 2.2	134.1 ± 5.0
Zr(tfa) ₄	sub	16	95-125	32.97	16066	$60302/T^2 - 309/T + 0.40$	133.6 ± 2.0	274.1 ± 5.3
Zr(tfa) ₄	vap	6	130-140	20.14	10913	$295335/T^2 - 1448/T + 1.77$	90.7 ± 4.5	167.4 ± 11.2
Zr(aa) ₄	sub	4	130-160	30.07	16690	$201430/T^2 - 964/T + 1.15$	138.8 ± 4.0	255.4 ± 9.1

culated from the mass loss data were much greater than those determined from the rise in mass in the cold zone. The latter values were used to calculate the saturated vapour pressure. Thus, it was assumed that all the investigated compounds vaporize in a monomolecular form. In the whole temperature range, the vapour pressure results obtained did not depend on the helium flow rate in the interval 0.5–2.0 l/h or on the duration of the experiment (within the limits of error). This indicated that the vaporization processes proceeded under quasi-equilibrium conditions (i.e. in this system saturation is reached and the influence of vapour diffusion is small).

The saturated vapour pressures of $Zr(pta)_4$, $Zr(dpm)_4$ and $Zr(hfa)_4$ were studied by a static method with a silica-membrane zero gauge. The technique of the experiment and installation was described in [5]. The maximum errors of temperature and pressure measurements were $\pm 0.5^\circ\text{C}$ and ± 0.2 Torr, respectively. The data obtained were reduced to standard conditions. The errors determined from the saturated vapour pressures of naphthalene and mercury were taken into account for temperature values.

Experimental data from the static method and the flow method, processed as in [6], are presented as the equation $\ln P$ (bar) = $B - A/T$ in Table 2. The standard thermodynamic parameters ΔH_T° and ΔS_T° for the processes of vaporization were calculated from the temperature dependences of the saturated vapour pressure for the investigated complexes.

For tensiometric studies, compounds subjected to 2–3 sublimations in the vacuum gradient furnace were used. The substances were additionally sublimed directly inside the manometer, in order to attain a pressure resulting from the desorption of gases from the sample surface.

Results and discussion

Curves of mass loss for Zr(IV) β -diketonates in vacuum, obtained in [7], are presented in Fig. 1. The qualitative range of volatility of Zr(IV) β -diketonates (for 20% mass loss) is: $Zr(hfa)_4$ (423 K) < $Zr(tfa)_4$ (483 K) < $Zr(pta)_4$ (523 K) < $Zr(aa)_4$ (decomposes) < $Zr(dpm)_4$ (583 K). It is impossible to draw strict conclusions about the volatility of the investigated compounds from these data because processes of sublimation and decomposition proceed simultaneously in many cases (e.g. $Zr(aa)_4$ and $Zr(tfa)_4$) at the beginning of the experiment. More exact data were obtained from measurements of the saturated vapour pressures of the investigated compounds.

Figure 2 depicts the temperature dependences of the saturated vapour pressures of the complexes of Zr(IV) with β -diketones investigated in the present work together with earlier published data. The obtained series of volatility is customary for complexes of metals(III) and metals(IV) [8, 9], though the difference in volatility between $Zr(aa)_4$ and $Zr(dpm)_4$ is somewhat less than for

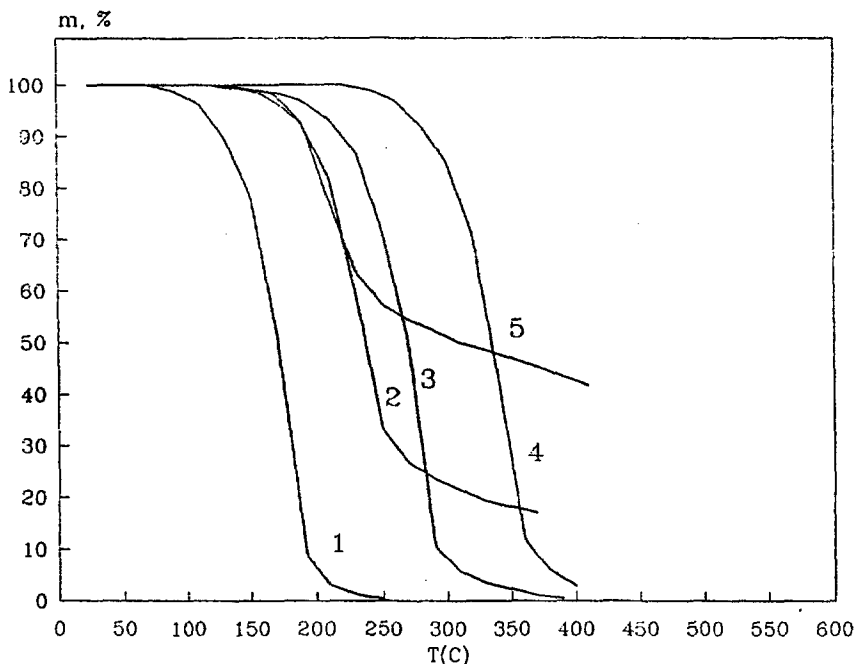


Fig. 1 Curves of mass loss of Zr(IV) β -diketonates in vacuum: Zr(hfa)₄ (1), Zr(tfa)₄ (2), Zr(pta)₄ (3), Zr(dpm)₄ (4) and Zr(aa)₄ (5)

complexes of metals(III). This can probably be explained by the significant increase in the molecular weight. A similar effect was observed earlier only for similar complexes of aluminium(III) [10]. It is readily observed from the presented data that the introduction of a trifluoromethyl group increases the volatility, which is usual for this class of compounds [8]. However, it should be noted that on the transition to hexafluoroacetylacetonates for complexes of metals(II) the volatility increases by 4–5 orders [11], for complexes of metals(III) by 3–4 orders [11], and for complexes of metals(IV) by 3 orders. The main reason for this difference is the increase in mass of the molecules and the increase in symmetry, which causes decreases in the differences in energy of intermolecular interactions in a crystal.

Attempts to measure the temperature dependence of the saturated vapour pressure for Zr(tfa)₄ by the static method with a silica-membrane zero gauge appeared to be unsuccessful because the temperature interval of measurement was very narrow (130–147°C). Besides, there was inevitably a residual pressure in the system, due to partial decomposition. The complex was therefore investigated by the flow method.

To obtain more precise results, the complex of Zr(pta)₄ was investigated both by the flow method and by the static method with a silica-membrane zero gauge.

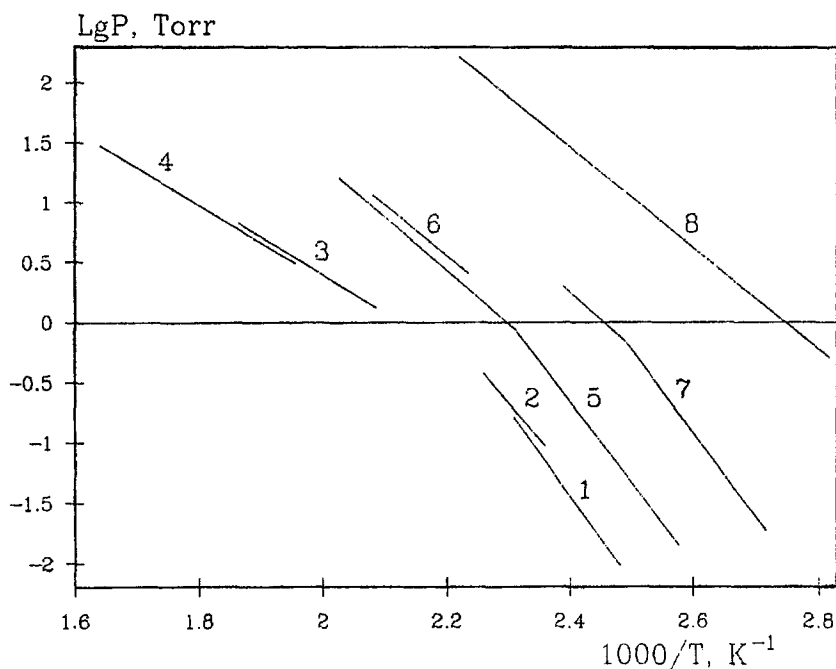


Fig. 2 Dependences of logarithm of saturated vapour pressure on reciprocal temperature for the complexes $Zr(aa)_4$ (flow) (1), $Zr(aa)_4$ (lit.) (2), $Zr(dpm)_4$ (membr.) (3), $Zr(dpm)_4$ (lit.) (4), $Zr(pta)_4$ (flow) (5), $Zr(pta)_4$ (membr.) (6), $Zr(tfa)_4$ (flow) (7) and $Zr(hfa)_4$ (membr.) (8)

Table 2 shows that the thermodynamic characteristics obtained for the evaporation of this complex by the two methods agree well with one another. This fact proves the assumption of the monomolecular structure of the vapour of this compound. However, it should be noted that literature data on the parameters of evaporation and sublimation for $Zr(dpm)_4$ and $Zr(aa)_4$ do not agree with our data. The following evaporation and sublimation parameters were published for $Zr(dpm)_4$: ΔH_{vap} (kJ/mol) = 71.84 ± 2.26 , ΔS_{vap} (J/mol K) = 93.01 ± 04.23 [1]; and for $Zr(aa)_4$: ΔH_{sub} (kJ/mol) = 116 ± 38 and ΔS_{sub} (J/mol K) = 198 ± 65 [2]. As concerns $Zr(dpm)_4$, the difference in the obtained values of the vaporization parameters can be explained by a large error in the determination of temperature in [1]. As concerns $Zr(aa)_4$, it should be noted that the saturated vapour pressure data that we determined agree well with literature data obtained by a flow method with the use of a radioactive indicator. The large difference in the thermodynamic parameters of the sublimation process can be explained by the narrower temperature interval of the reported data [2] and the large error in its determination. Joint processing of our own and the literature experimental results gives the following dependence of vapour pressure on temperature in the interval 130–170°C:

$$\ln P \text{ (bar)} = 29.18 - 16318/T$$

The values of the thermodynamic functions of the sublimation process are as follows:

$$\Delta H_{\text{sub}}^{\circ} = 135.7 \pm 5 \text{ (kJ/mol)} \text{ and } \Delta S_{\text{sub}}^{\circ} = 243 \pm 11 \text{ (J/mol K)}$$

The following range of volatility of Zr(IV) β -diketonates is obtained from our saturated vapour pressure data (for $P=1$ Torr): Zr(gfa)_4 (364 K) $<$ Zr(tfa)_4 (407 K) $<$ Zr(pta)_4 $<$ (434 K) $<$ Zr(aa)_4 (451 K) $<$ Zr(dpm)_4 (472 K).

Thus, the results reported in the present work have allowed determination of the parameters of evaporation and sublimation for earlier investigated complexes of Zr(IV) with β -diketonates, and also for newly investigated β -diketonates of Zr(IV).

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