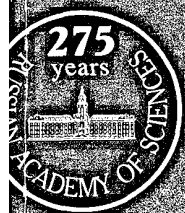


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# **RUSSIAN JOURNAL OF GENERAL CHEMISTRY**

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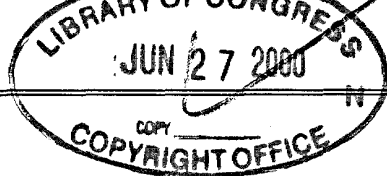
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# Thermal Stability of Zirconium Organic Derivatives with Ligands of Different Nature

E.I. Tsyganova, L.M. Dyagileva, and Yu.A. Aleksandrov

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**Abstract**—Specific features of kinetics and mechanism of thermal decomposition of zirconium organic derivatives with ligands of different nature (acetylacetone, dialkylamines, cyclopentadienyl or methyl groups, chloride ion) were studied. The nature of the Zr–element (Zr–C, Zr–O, Zr–N) bond has the principal effect on the kinetic features and mechanism of thermal decomposition.

Intensification of many industrial processes involves the necessity of maintaining high temperatures and mechanical loads, which inevitably requires the use of appropriate materials capable of retaining their principal service properties under extreme conditions.

Films of zirconium nitrides, carbonitrides, oxides, and carbides are promising materials for protecting metals from high-temperature oxidation, and nowadays they are widely used as thermal-barrier coatings with high abrasion resistance [1].

Due to their high volatility and oxidation resistance, zirconium organic derivatives with Zr–C, Zr–O, and Zr–N bonds are convenient starting compounds for preparing zirconium-containing coatings by chemical vapor deposition.

In this paper we summarize and correlate the results obtained in the course of studying the general trends in kinetic stability and mechanism of thermal decomposition of zirconium organic derivatives; their designations are given in Table 1.

Consider the effect of the ligand on the volatility, kinetic features, and mechanism of thermal decomposition of organozirconium compounds. All the zirconium derivatives in hand have sufficient vapor pressure within the temperature range studied. Compounds I, V, and VI are solids, I and V are stable to atmospheric oxygen, and VI is slowly hydrolyzed in air. Compounds II–IV are yellowish liquids and are also hydrolyzed in air. Published data on the temperature dependence of the saturated vapor pressure for I, V, and VI are presented in Table 2.

**Table 1.** Designations of zirconium organic derivatives

Compound no.	Compound name	Formula	Designation
I	Zirconium acetylacetonate	$\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$	$\text{Zr}(\text{acac})_4$
II	Zirconium tetrakisdiethylamide	$\text{Zr}[\text{N}(\text{C}_2\text{H}_5)_2]_4$	$\text{Zr}(\text{NEt}_2)_4$
III	Zirconium tetrakisdipropylamide	$\text{Zr}[\text{N}(\text{C}_3\text{H}_7)_2]_4$	$\text{Zr}(\text{NPr}_2)_4$
IV	Zirconium tetrakisdibutylamide	$\text{Zr}[\text{N}(\text{C}_4\text{H}_9)_2]_4$	$\text{Zr}(\text{NBu}_2)_4$
V	Biscyclopentadienylzirconium dichloride	$(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$	$\text{Cp}_2\text{ZrCl}_2$
VI	Biscyclopentadienyldimethylzirconium	$(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$	$\text{Cp}_2\text{ZrMe}_2$

**Table 2.** Coefficients A and B in the equation of temperature dependence of saturated vapor pressure  $\log P \text{ (hPa)} = B - A/T$

Compound no.	A	B	Temperature, K	References
I	$6050 \pm 20$	$13.32 \pm 0.25$	423–443	[2]
V	$2760 \pm 10$	$6.51 \pm 0.21$	473–505 (sublimation)	[3]
	$3360 \pm 30$	$7.61 \pm 0.51$	538–571 (vaporization)	
VI	$1803 \pm 66$	$5.54 \pm 0.27$	413–453	[4]

With respect to volatility, the compounds can be ranked in the following order:  $\text{Cp}_2\text{ZrMe}_2 > \text{Zr}(\text{acac})_4 > \text{Cp}_2\text{ZrCl}_2$ .

The kinetic and activation parameters of thermal decomposition of the zirconium compounds under study are given in Table 3. Also given are the temperature range of thermal decomposition and the initial pressure region in which thermal decomposition was studied [2–5].

The kinetic parameters were measured manometrically under static conditions *in vacuo* by the procedure described in detail in [6].

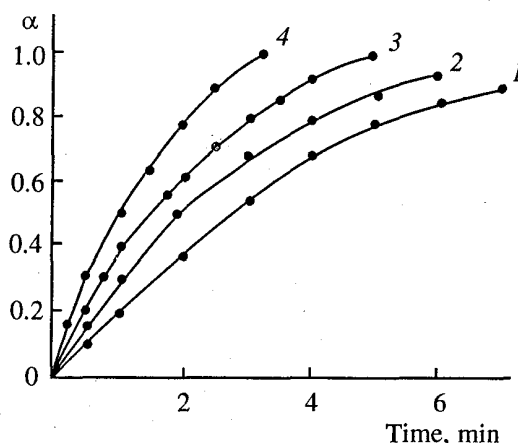
Except  $\text{Cp}_2\text{ZrMe}_2$ , all the compounds studied decompose in the gas phase by a first-order reaction with respect to both running and initial concentrations of the starting compound. Typical kinetic curves are shown in Fig. 1 for the case of thermal decomposition of  $\text{Zr}(\text{acac})_4$ . Thermal decomposition of  $\text{Cp}_2\text{ZrMe}_2$  took place both in the liquid (446–488 K) and in the gas phase (498–550 K).

At 446–488 K the kinetic curves of mainly liquid-phase decomposition of  $\text{Cp}_2\text{ZrMe}_2$  in the  $\alpha = f(t)$  coordinates are S-shaped with an induction period followed by a section with a noticeable initial rate (up to 10% decomposition) and then by the section in which the gas evolution proceeds at the maximal rate (Fig. 2). The induction period tends to decrease with increasing temperature and totally disappears at 498 K [4]. For  $\text{Cp}_2\text{ZrMe}_2$  the initial rates of gas evolution were calculated by graphical differentiation of the kinetic curves at the conversion  $\alpha$  0.05. At 513–550 K mainly gas-phase decomposition of  $\text{Cp}_2\text{ZrMe}_2$  was observed. In this case only fully developed process with the highest gas evolution rate was observed in the kinetic curves  $\alpha = f(t)$ . The activation energy of this process is 41 kJ mol<sup>-1</sup>, which suggests that gas-phase decomposition of  $\text{Cp}_2\text{ZrMe}_2$  is nearly diffusion-controlled.

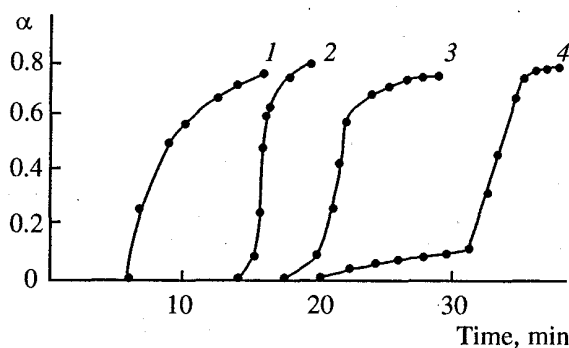
**Table 3.** Kinetic and activation parameters of thermal decomposition of organic derivatives of zirconium (glass ampoules 50–75 cm<sup>3</sup> in volume,  $S/V$  1.5 cm<sup>-1</sup>)

Comp. no.	$P_0$ , hPa	$T$ , K	$E_a$ , kJ mol <sup>-1</sup>	$\log K_0$	$k \times 10^3$ , s <sup>-1</sup> (523 K)	References
I	52–133	523–558	$53.5 \pm 1.7$	$3.02 \pm 0.15$	4.4	[2]
II	26.6–186.2	513–623	$69.8 \pm 3.7$	$4.13 \pm 0.38$	1.27	[5]
III	26.6–186.2	513–593	$74.9 \pm 3.4$	$4.59 \pm 0.33$	1.15	[5]
IV	26.6–186.2	513–553	$125.3 \pm 3.4$	$9.55 \pm 0.81$	0.83	[5]
V	66–133	778–813	$250 \pm 2.9$	$12.9 \pm 1.9$	$5.5^a$	[3]
VI <sup>b</sup>	<sup>c</sup>	446–488	$189.4 \pm 6.3$	$19.9 \pm 0.7$	—	[4]

<sup>a</sup>  $\times 10^{10}$ . <sup>b</sup> Kinetic parameters were calculated from the rate of the liquid-phase decomposition  $[W]$ , min<sup>-1</sup> at  $\alpha$  0.05. <sup>c</sup>  $(2.3\text{--}3.0) \times 10^{-3}$  M.



**Fig. 1.** Kinetic curves of thermal decomposition of zirconium acetylacetonate. Temperature, K: (1) 523, (2) 533, (3) 550, and (4) 558.



**Fig. 2.** Plots of the degree of decomposition of bis-(cyclopentadienyl)dimethylzirconium vs. time at temperature, K: (1) 488, (2) 473, (3) 458, and (4) 446.

With respect to thermal stability, as judged from the rate constant of thermal decomposition, the zirconium compounds under study can be ranked in the following order:  $\text{Cp}_2\text{ZrCl}_2 > \text{Zr}(\text{NBu}_2)_4 > \text{Zr}(\text{NPr}_2)_4 > \text{Zr}(\text{NEt}_2)_4 > \text{Zr}(\text{acac})_4 > \text{Cp}_2\text{ZrMe}_2$ .

**Table 4.** Average bond energy ( $E_b$ ) in zirconium organic compounds

Comp. no.	Bond	$E_b$ , kJ mol <sup>-1</sup>	References
VI	Zr-Me	274±5	[7]
	Zr-Cp	358±5	
	Zr-NMe <sub>2</sub>	343±8	
II	Zr-NEt <sub>2</sub>	356±8	[8]
V	Zr-Cp	358±4	[7]
	Zr-Cl	488±2	
	C-H	263±2	

**Table 5.** Effect of the heterogeneity factor ( $S/V$ ) and pyrolysis products on the rate constant of thermal decomposition of zirconium organic derivatives

Comp. no.	T, K	$S/V$ , cm <sup>-1</sup>	Coating	$k \times 10^3$ , s <sup>-1</sup>	References
I	523	1.5	Glass	4.4	[2]
	523	10	"	4.4	
	523	1.5	Solid thermolysis products <sup>a</sup>	8.0	
II	533	1.8	Glass	1.8	[5]
	533	15	"	0.6	
	533	1.8	Solid thermolysis products <sup>a</sup>	4.6	
	553	1.8	Glass	3.6	
	553	15	"	1.9	
	553	1.8	Solid thermolysis products <sup>a</sup>	5.8	
III	553	1.8	Glass	1.7	[5]
	553	15	"	0.8	
	553	1.8	Solid thermolysis products <sup>a</sup>	5.6	
IV	553	1.8	Glass	1.52	[5]
	553	15	"	0.6	
	553	1.8	Solid thermolysis products <sup>a</sup>	4.5	
V	793	1.5	Glass	0.29	[3]
	793	15	"	0.87	
	793	1.5	Solid thermolysis products <sup>a</sup>	0.91	

<sup>a</sup> The solid thermolysis products of the given compound were obtained in the previous run at the same temperature, kept in air, and freed of adsorbed liquid and gaseous products by keeping *in vacuo* at the temperature of the experiment.

The above order of thermal stability is in a good agreement with the average bond energies in zirconium compounds determined by thermodynamic methods [7, 8] (Table 4). It can be thus concluded that introduction of a powerful electron-withdrawing

chlorine atom into a molecule of an organozirconium compound and the appearance of the highly polar Zr-Cl bond, on the one hand, results in decreased volatility of V and, on the other hand, leads to its increased thermal stability.

Data on bond energies in Zr(acac)<sub>4</sub> are lacking. It is only known that the M-O bond energy in acetylacetonates is estimated to be 160–280 kJ mol<sup>-1</sup> and is the weakest in the chelate molecule [9]. In alkylamide derivatives of zirconium a slight increase in the bond energy is observed with increasing length of the alkyl substituent [8].

Pyrolysis of the zirconium organic compounds in hand is a complex homogeneous-heterogeneous process. No unequivocal relationship between the rate constant and the heterogeneity factor  $S/V$  ( $S$  is the surface area of the reactor,  $V$  is its volume) was observed (Table 5). In the case of Zr(acac)<sub>4</sub> the tenfold increase in  $S/V$  had no effect on the rate constant of thermal decomposition. With zirconium alkylamide derivatives the rate constant of thermal decomposition regularly decreased with increasing heterogeneity factor. An increase in  $S/V$  by a factor of 5–8 results in a decrease in the rate constant by a factor of 1.5–3. In the case of Cp<sub>2</sub>ZrCl<sub>2</sub> the rate constant increased with increasing surface area, which is typical for thermal decomposition of organometallic compounds [6].

Coating of the walls of the reaction vessel with solid thermolysis products resulted for all the examined compounds in increase in the rate constant by a factor of 2–3, which is indicative of the significant contribution of heterogeneous stages to decomposition.

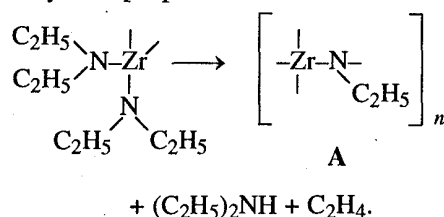
Thermolysis of the zirconium compounds in hand yields solid, liquid, and gaseous products. The mechanism of thermal decomposition of zirconium organic derivatives is determined by the nature of the zirconium–element bond (Zr–C, Zr–O, Zr–N) and by the relative bond energies in the ligand (Table 4).

Specific features of thermal decomposition of Zr(acac)<sub>4</sub> [2] arise from the presence of two reaction centers, namely, the Zr–O bond and  $\gamma$ -CH proton in its molecule. It was suggested that the first stage of thermal decomposition of Zr(acac)<sub>4</sub> is opening of the chelate ring by transformation of the bidentate ligand into a monodentate one, followed by decomposition by various routes. Also possible are steric rearrangement of the ligand and transfer of the  $\gamma$ -CH proton of the nonactivated ligand onto the activated ligand resulting in the formation of a free ligand as a neutral species, and also cleavage of intramolecular bonds in the chelate ligand leading to the formation of volatile low-molecular-weight products [10].

The composition of the products of complete decomposition of  $\text{Zr}(\text{acac})_4$  at 623 K (acetone 60,  $\text{CO}_2$  17.8, CO 21.7, acetylacetone 0.2 mol %, respectively) suggests that the second direction is the main decomposition pathway.

Of the alkylamide derivatives of zirconium the following main stages of thermal decomposition are characteristic [5]: (1) cleavage of the Zr–N bond resulting in the elimination of dialkylamine and (2) cleavage of the N–C bond leading to the liberation of alkene. These two stages are interrelated. Formation of dialkylamine by thermal decomposition of zirconium tetrakisdialkylamides requires hydrogen, which can be abstracted from the neighboring alkyl group. This is evidenced by the fact that the products of hydrolysis of these compounds contain alkene (or its transformation products) and amine in nearly equal amounts.

As an example, for ethyl derivatives the following scheme may be proposed.



The final product of this transformation is polymeric product A, and at temperatures above 673–773 K this phase is a basis for the formation of zirconium nitride or carbonitride.

Thermal decomposition of  $\text{Cp}_2\text{ZrCl}_2$  proceeds by a molecular pathway in two directions: by cleavage of the Zr–Cp bond and C–H bond in the cyclopentadienyl fragment [3].

In the early stages of decomposition cyclopentadiene is the principal thermolysis product; under the given experimental conditions it subsequently undergoes catalytic decomposition on the zirconium-containing coating to give hydrogen and methane. Their proportion in the products grows with temperature. No chlorine-containing gaseous compounds were detected. The solid thermolysis product was a metal-cross-linked polymer  $[\text{C}_5\text{H}_5(\text{C}_5\text{H}_5-n)\text{Zr}]_m$  depleted of hydrogen. Heating of this product results in the loss of hydrogen and formation of zirconium carbide. Under the examined experimental conditions the Zr–Cl bond is not cleaved, and chlorine in the thermolysis products is in the form of  $\text{ZrCl}_4$ .

The predominant decomposition pathway of  $\text{Cp}_2\text{ZrMe}_2$  is cleavage of the  $\sigma$  bond Zr–Me, which is weaker than the  $\pi$  bond Zr–Cp (Table 4). As no products of dimerization of methyl radicals were

detected, it is assumed that cleavage of the Zr–Me bond and formation of the Me–H bond follow a molecular pathway, without formation of free methyl radicals.

The formation of the principal product, methane, involves simultaneous cleavage of the  $\sigma$  bond Zr–Me as well as the C–H bonds in the five-membered ring and the methyl group. The main direction of decomposition, cleavage of the  $\sigma$  bond Zr–Me, is accompanied by partial cleavage of the C–H bonds of the cyclopentadienyl group, which results in evolution of hydrogen along with methane. Under more rigorous conditions (temperature, pressure, catalyst) stronger Zr–Cp bonds may also be cleaved to give cyclopentadiene.

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