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Vapor pressure and crystal lattice energy of volatile palladium(II) β-iminoketonates

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Abstract Volatile palladium(II) β-iminoketonates of the general formula Pd(R–C(NH)–CH–CO–R^1),where R and R^1 are CH_3, CF_3, $C(CH_3)_3$ in various combinations, were synthesized and identified. Thermal properties of the resulting palladium(II) complexes in the solid phase were studied by thermogravimetric analysis under an argon atmosphere. The temperature dependence of the saturated vapor pressure was measured for the compounds by the flow method and thermodynamic characteristics of vaporization processes, enthalpy ΔH_T and entropy ΔS^o_T, were determined. The atom-atomic potential calculation of the van der Waals energy (E_{cryst}) of the crystal lattice was performed and the results were compared to the experimental values of the sublimation enthalpy for the complexes under study.

Keywords β-Ketoiminate Pd(II) · Thermogravimetric investigation · Vapor pressure · Volatile · Energy of a lattice

Introduction

The palladium film deposition on various surfaces by the MO CVD method is being extensively investigated [1, 2]. The problem of the metal deposit production with using the volatile palladium complexes requires both a search of novel precursors and the prediction of the volatility, that is, the transition to the gas phase with the molecular unit unchanged. The volatile palladium(II) β-diketonates of the molecular structure, the most suitable for CVD processes, have been studied by us [3, 4]. The volatility and thermal stability of those in condensed and gas phases vary over a wide range depending on the ligand substituent and the type of the chelate constituent. Metal β-diketonates are known to be representatives of chelate compounds forming the molecular crystals with the molecules linked by the weak van der Waals forces [5–7], therefore the estimation of the interaction energy provides the basis for the prediction of the volatility in the compounds of the given class.

The atom-atomic potentials method (AAP) may be used for the calculation of the van der Waals interaction energy in the molecular crystals of organic compounds, as reported in detail in [8–10]. The molecule packing and the intermolecular interactions were considered for a number of palladium(II) and iridium (I) β-diketonates and the van der Waals energy of the crystal lattice was calculated by us [11, 12].

To continue the research, the volatile palladium(II) β-iminoketonates are of interest, which differ from the β-diketonates by the substitution of one oxygen atom for the NH-group in the ligand. In the CVD processes, the metal β-iminoketonates may have an advantage over the β-diketonates, as they contain a less number of the oxygen atoms in the chelate molecule, resulting in a diminution of the substrate layer oxidation upon the metal film production. It should be noted that the palladium(II) β-iminoketonates are not practically studied in literature and mentioned only in two works [13, 14]. The unit cell parameters and infrared spectra for the first specimen of this class of the compounds, $Pd(acac)_2$, were reported in Refs. [13] and [14], respectively. The crystal structure of this coordination compound has been recently solved by us [15]. The palladium(II) β-iminoketonates of the general formula $Pd(R–C(NH)–CH–CO–R^1)_2$, where R and R^1 are

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CH_3, CF_3, $C(CH_3)_3$ in various combinations, were first obtained and studied [15–18].

This paper reports a new technique of the synthesis of the palladium(II) β-iminoketonates based on different aminovinylketones. The behavior of the complexes on heating under an inert atmosphere was studied by thermogravimetry. The temperature dependence of the saturated vapor pressure was measured by the flow method and the standard thermodynamic parameters ΔH_T and ΔS_T^o were determined for the vaporization process of the compounds. The molecule packing in the crystals was considered using the structural data and the van der Waals energy of the crystal lattice (E_{cryst}) was calculated for these complexes.

Experimental

Synthesis of Pd complexes

For the synthesis of the β-iminoketonate complexes Pd (R–C(NH)–CH–CO–R^1)$_2$ with a high yield we have used a new procedure [16] based on the interaction between the $PdCl_2$ salt and the (HL) ligands in the medium of appropriate amine according to the following scheme:

$$PdCl_2 \xrightarrow{excessNH_2R(solv)} \left[Pd(NH_2R)_4\right]Cl_2 \xrightarrow{+2HL,pH=8-9} PdL_2,$$

where R = H or CH_3.

The reaction occurs via formation of an intermediate colorless $[Pd(NH_2R)_4]Cl_2$ complex in solution, which further reacts with the ligand.

The $PdCl_2$ sample (1 g, 5.6 mmol) placed in the ammoniate solution (25 mL of water and 25 mL of the concentrated ammonia solution) was heated on a water bath until the salt was completely dissolved, resulting in the colorless solution (pH should be kept at a high alkaline level). Then the proper HL ligand (11.2 mmol) dissolved in 20 mL of ethanol was added to the solution. With increasing the temperature of the reaction mixture, its pH decreased and Pd(L)$_2$ began to precipitate at pH = 8–9. The precipitate was filtered off, washed with water, dried in air, and dissolved in benzene. The product isolated from benzene was purified by vacuum sublimation (T = 200 °C, $P = 10^{-2}$ Torr). The yield of the sublimated products was 70–80%. The β-iminoketonate complexes are yellow crystalline powders dissolving in common organic solvents. The characteristics of the complexes and used ligand formulas are given in Table 1.

Thermal investigation

TG measurements were carried out on a Netzsch TG 209 F1 thermal analyzer under an argon flow (40 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The temperature range was 20–350 °C, the open crucibles were standard, and the sample mass was taken to be ca. 2–3 mg. Melting points were determined with the Koffler apparatus.

Vapor pressure

The saturated vapor density of the above palladium(II) β-iminoketonates was measured with a flow method in atmosphere of a dry inert gas carrier (helium). We have used this technique to measure the saturated vapor pressure of volatile complexes of the platinum group metals [19]. The starting materials were previously purified by the sublimation.

The amount of the substance vaporized on the passage of certain helium volume with the following condensation in a cold zone was determined by weighing. The total error of this method was no more than 5% with the accuracy concerning the temperature ±0.5° and the error in the measurement of the flow rate ±2%. The measurements were carried out in quasi-equilibrium conditions. The independence of the vapor pressure on the helium flow rate was the experimental evidence of this statement. The application of the flow method to study this class of compounds is very useful because it allows measuring the reliable low vapor pressure values against a background of partial thermal decomposition of the compound. The saturated vapor pressure was calculated using:

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

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

Table 1 Characteristics of palladium(II) β-iminoketonates

Compound Pd(L)$_2$	R–C(NH)–CH–CO–R^1		Found/%			Calc./ %			M.p./°C
	R	R^1	C	H	N	C	H	N	
Pd(i-acac)$_2$	CH_3	CH_3	39.52	5.18	9.45	39.68	5.33	9.26	245
Pd(i-tfac)$_2$	CH_3	CF_3	29.40	2.61	6.64	29.20	2.43	6.82	214
Pd(i-ptac)$_2$	$C(CH_3)_3$	CF_3	38.50	4.62	5.83	38.80	4.45	5.66	<250
Pd(i-dpm)$_2$	$C(CH_3)_3$	$C(CH_3)_3$	56.29	8.42	6.22	56.10	8.56	5.95	270
Pd(mi-acac)$_2$	CH_3–C(NCH_3)–CH–CO–CH_3		43.37	6.24	8.24	43.58	6.10	8.47	<195

The calculation is based on the assumption that the substance vaporizes in the monomolecular form. It should be noted that the results obtained both on the loss in mass of the substance and the rise in mass of the condensed substance in the cold zone practically coincided. This indicates that the complex possesses the thermal stability within the studied temperature range. An exception is the substance Pd(mi-acac)$_2$, which decomposes partially when transferred to the gaseous phase.

Calculations of intermolecular interaction energy

The van der Waals energy of the intermolecular interaction in the crystals was calculated using the structural data for the complexes [15–18] available from the CSDB (Cambridge Structural Database).

The Buckingham potential parameters for the AAP calculations were taken from [20]. The van der Waals interaction energy was calculated as:

$$E_{\mathrm{crys}} = 1/2\sum_{k=2}^{N}\sum_{i=1}^{n}\sum_{j=1}^{n}\left[-A_{i,j}/R_{i,j}^{6} + B_{i,j}\cdot\exp(-\alpha_{i,j}\cdot R_{i,j})\right],$$

where k is the neighboring molecule number, N is the quantity of the nearest molecules, i is the number of atom in the first molecule, j is the number of atom in the k-molecule, n is the quantity of the atoms in the molecule, $R_{i,j}$ is the distance between i and j atoms; $A_{i,j}$, $B_{i,j}$, $\alpha_{i,j}$ are the parameters of the atom-atomic potential

For all palladium complexes considered, the calculated van der Waals energies (E_{cryst}) and experimental sublimation enthalpies (ΔH_{subl}) are reported in Tables 2 and 3.

Results and discussion

TG study

The TG curves of the mass loss for the Pd(II) compounds on heating under an inert atmosphere are shown in Fig. 1. At these conditions, the vaporization process of the PdL$_2$ complexes proceeds with minimal decomposition (no more than 10–15%), indicating their high thermal stability. On the basis of the analysis of the mass loss curves in inert atmosphere the row demonstrating volatility decreasing of Pd(II) compounds is obtained:

$$\mathrm{Pd(i\text{-}tfac)_2} > \mathrm{Pd(i\text{-}ptac)_2} > \mathrm{Pd(mi\text{-}acac)_2} > \mathrm{Pd(i\text{-}dpm)_2} > \mathrm{Pd(i\text{-}acac)_2}.$$

The thermoanalytical study of the palladium β-iminoketonates showed that the substitution of the NH group by the NCH$_3$ group in the chelate unit resulted in the significant rise in the volatility of the Pd(mi-acac)$_2$ complex as compared to Pd(i-acac)$_2$.

Vapor pressure

Experimental data on the gas flow method, processed by a special technique [21], are represented by the $\ln P = A - B/T$ ratio. The temperature dependences of the saturated vapor pressure for those compounds were used to derive the standard thermodynamic parameters ΔH_{T} and $\Delta S_{\mathrm{T}}^{\circ}$ of the sublimation within the average temperature intervals (Table 2). Figure 2 presents the temperature dependences of the vapor pressure for the solid Pd(II) chelate complexes.

The consideration of the $\ln P - 1/T$ dependences shows that the type of the chelate core in the complexes less affects the volatility than the introduction of the CF$_3$ group into the ligand. The experimental results support the revealed general downward drift of the volatility of the palladium complexes by the introduction of the CF$_3$ groups into the ligand. Among the compounds studied, the most volatile one is the complex containing fluorinated group substituents in the ligand. Rather unexpected, in our opinion, is a significant difference in the volatility between Pd(i-acac)$_2$ and Pd(mi-acac)$_2$ complexes. The latter, having the lower thermal stability, appeared to be more volatile than Pd(i-acac)$_2$. The steric factors are likely of importance here preventing the palladium atom from the interaction with the neighboring molecules that results in decreasing the intermolecular interactions.

Table 2 Thermodynamic parameters of palladium(II) compounds sublimation processes (flow technique)

Compound	n[a]	T/K	Ln(P/atm) ± σ = A − B/T			$-\Delta H_{\mathrm{T}}$/kJ mol^{-1}	$\Delta S_{\mathrm{T}}^{\circ}$/J (mol K)$^{-1}$
			A	B	σ^2		
Pd(i-tfac)$_2$	7	382–443	23.94	13439	$5 \times 10^4/T^2 - 240/T + 0.3$	112 ± 2	199 ± 4
Pd(i-ptac)$_2$	11	381–453	26.65	14698	$7 \times 10^4/T^2 - 330/T + 0.4$	122 ± 2	222 ± 5
Pd(mi-acac)$_2$	7	382–443	22.15	13038	$9 \times 10^5/T^2 - 4 \times 10^3/T + 5$	108 ± 8	184 ± 20
Pd(i-dpm)$_2$	18	403–483	23.91	14747	$2 \times 10^5/T^2 - 730/T + 0.8$	123 ± 3	199 ± 8
Pd(i-acac)$_2$	8	453–513	25.64	16992	$4 \times 10^5/T^2 - 2 \times 10^3/T + 2$	141 ± 6	213 ± 11

[a] n is the number of experimental points

Table 3 Calculation of intermolecular van der Waals interaction energy in crystals

Compound	M.W./g mol^{-1}	Space group	Z	Ref.	Packing type	$-E_{\mathrm{cryst}}$/kJ mol^{-1}	$-\Delta H_T$ (exp.)/kJ mol^{-1}
Pd(i-tfac)$_2$	410.6	P2$_1$/n	2	[16]	Stack	98.0	112 ± 2
Pd(i-ptac)$_2$	494.7	P-1	1	[17]	Stack	127.4	122 ± 2
Pd(mi-acac)$_2$	330.7	P1	1	[15]	Stack	117.7	108 ± 8
Pd(i-dpm)$_2$	471.0	P2$_1$/n	2	[18]	Net	136.1	123 ± 3
Pd(i-acac)$_2$	302.6	Ccca	12	[15]	Band	133.2	141 ± 6

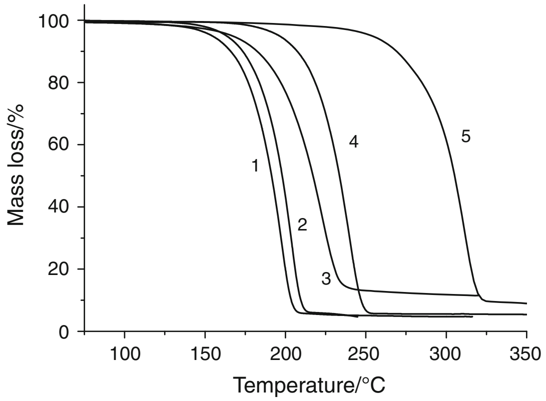

Fig. 1 TG profiles for for the complexes: *1* Pd(i-tfac)$_2$, *2* Pd(i-ptac)$_2$, *3* Pd(mi-acac)$_2$, *4* Pd(i-dpm)$_2$, *5* Pd(i-acac)$_2$

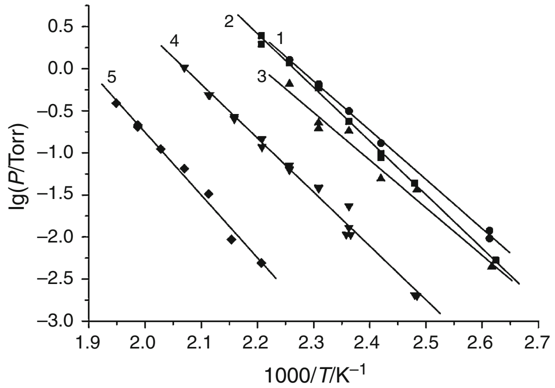

Fig. 2 Dependencies of logarithm of saturated vapor pressure reciprocal temperature for the complexes: *1* Pd(i-tfac)$_2$; *2* Pd(i-ptac)$_2$; *3* Pd(mi-acac)$_2$; *4* Pd(i-dpm)$_2$; *5* Pd(i-acac)$_2$

Van der Waals energy of the lattice and molecule packing

The calculated van der Waals interaction energy values (E_{cryst}) and the experimental sublimation enthalpy values (ΔH_{subl}) are given in Table 3. E_{cryst} are scattered around the experimental ΔH_{subl} of the compounds but differ by no more than 10%, suggesting a good fit between those. The consideration of the molecule packing in the crystals shows that the packing type influences the volatility of the compounds. The molecules are similarly packed in the stacks in both the Pd(i-tfac)$_2$ and Pd(i-ptac)$_2$ crystals and this is true for the complex Pd(mi-acac)$_2$. In such stacks, each molecule intensively interacts with two neighbors. The increased volatility of the fluorinated complexes is explained by a weaker intermolecular interaction between the molecule stacks in the crystal [11]. There are four bulk *tert*-butyl substituents which significantly screen the palladium atom from the interaction with the neighboring molecule atoms. In this case, the molecules are packed in the nets. In the crystal of Pd(i-acac)$_2$, the complexes form the ribbons in which the molecules have two nearest neighbors each with the molecule planes rotated by 60°. The rotation results in approaching the molecule centers and allows the donor N and O atoms of the neighboring molecules to be closer to the palladium atom thus increasing the interaction between the molecules. This is just the reason for the Pd(i-acac)$_2$ complex to have the lower volatility than Pd(mi-acac)$_2$ has in which the presence of the CH_3 group nearby the nitrogen atom prevents the palladium atom from being interacted with the neighboring molecules. This conclusion fits the thermal characteristics of these complexes well (Table 3; Fig. 1).

Conclusions

The work deals with the synthesis of the Pd(L)$_2$ complexes with a high product yield. On the basis of the analysis of the mass loss curves in inert atmosphere the row demonstrating volatility decreasing of Pd(II) compounds is obtained: Pd(i-tfac)$_2$ > Pd(i-ptac)$_2$ > Pd(mi-acac)$_2$ > Pd(i-dpm)$_2$ > Pd(i-acac)$_2$.

The temperature dependence of the saturated vapor pressure was measured and the thermodynamic parameters of the sublimation process were calculated. The molecule packing in the crystals and the intermolecular contacts are considered based on the structural data. The van der Waals lattice energies were calculated and compared to the experimental sublimation enthalpy values of the complexes.

Due to high volatility and thermal stability the palladium(II) β-iminoketonates studied in this work can be used as precursors in CVD processes for the production of palladium films for various purposes.

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