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Thermodynamic Characteristics of the Cadmium Pivalate Phenanthroline Complex $Cd_2Piv_4Phen_2$

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Abstract—Evaporation of the cadmium pivalate phenanthroline complex $Cd_2Piv_4Phen_2$ was studied by the Knudsen effusion method with mass spectral analysis of gas phase composition. The evaporation is congruent, and the gas phase consists of $CdPiv_2Phen$ molecules. The standard enthalpy of sublimation of these molecules was found. The energy of dissociation of $CdPiv_2Phen$ molecules to cadmium pivalate and phenanthroline was determined on the basis of experimental data on ionization.

Keywords: mass spectrometry, cadmium pivalate phenanthroline complex, thermodynamics

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INTRODUCTION

Cadmium oxide, like zinc, indium, and tin oxides, belongs to the group of transparent conducting oxides (TCO) and, because of its electrical, optical, chemical, and physicochemical properties, it is fairly promising as a working medium for the design of analytical instruments, sensors, transistors, field emission displays, etc. [1–3]. In recent years, interest was aroused in multicomponent electrically conducting systems containing cadmium oxide such as CdO–In2O3–SnO2 [4] and CdO–ZnO–SnO2 [5]. In their electrical, optical, and catalytic properties, thin films of complex oxides based on these systems can compete with indium tin oxide (ITO), which is the most demanded TCO material. Functional film materials based on the above-listed multicomponent oxide systems can be prepared by chemical vapor deposition (CVD) in which volatile complexes of trimethylacetic acid were used as precursors.

A preliminary investigation of a polymeric cadmium pivalate has shown that evaporation of this compound is accompanied by complete thermal decomposition to give cadmium atoms, carbon dioxide, and carbonyl, carboxyl, and other gaseous products. Note that this situation is expected in the case where the enthalpy of polymerization of the complex molecules in the condensed phase is markedly higher than the enthalpy of their vaporization. An approach that allows one to suppress polymerization of the condensed phase and thus to obtain volatile compounds to be used as CVD precursors consists in saturation of the central ion coordination sphere with additional ligands such as *o*-phenanthroline (Phen), tri(*n*-butyl)phosphine, bipyridine and so on [6–8]. Evaporation of this complexes can be either incongruent, with the additional ligand migrating to the gas phase in the first stage and the unpolymerized major component being vaporized later at higher temperature [7–9], or congruent with partial dissociation or sublimation as a single complex molecular species [6, 10].

This study is concerned with vaporization pro-cesses and thermodynamic characteristics of the cadmium pivalate phenanthroline complex $Cd_2Piv_4Phen_2$ (**I**).

EXPERIMENTAL

Compound **I** was synthesized by a reported procedure [11]. 1,10-Phenanthroline monohydrate (0.063 g, 0.318 mmol) was added to a vigorously stirred solution of $[Cd(Piv)_2]$ (0.100 g, 0.318 mmol) in 15 mL of acetonitrile at 60°C. After 5 min, a colorless finely crystalline solid precipitated from the solution. The reaction mixture with the precipitate was stirred for 1 h with heating ($T = 60$°C). The precipitate was collected on a filter, washed with MeCN, and dried in air. After 3 h, slow evaporation of the mother liquor in air gave colorless crystals suitable for mass spectral thermodynamic measurements. The yield was 0.120 g (77%) in relation to the initial amount of $[Cd(Piv)_2]$.

The composition of the product was confirmed by C,H,N-analysis carried on a EuroVector 300 CHN-analyzer at the Center for Collective Use of the Insti-

Table 1. Results of CHN analysis of samples obtained in a vacuum post system

Element	Sample no. 1 (T = 470 K)	Sample no. 2 (T = 500 K)	Sample no. 3 (T = 270 K)	Calculated for $CdPiv_2Phen$
C	52.1	51.2	52.2	53.4
H	5.2	5.2	5.2	5.3
N	5.9	5.8	6.1	5.7

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For $CdPiv_2Phen$

Anal. calcd., %	C, 53.4	H, 5.3	N, 5.7
Found, %	C, 53.7	H, 5.6	N, 5.7

The IR spectrum of the complex was measured on a Perkin Elmer Spectrum 65LS FT IR spectrophotometer (ν, cm^{-1}): 3057 m, 2950 s, 2922 m, 2864 m, 1547 vs, 1509 s, 1494 m, 1478 s, 1456 m, 1411 vs, 1372 s, 1357 s, 1341 m, 1221 s, 1191 m, 1144 w, 1101 m, 1027 w, 937 w, 896 m, 862 m, 847 s, 809 m, 791 m, 779 m, 724 s, 637 m, 599 m, 532 m, 418 w.

RESULTS AND DISCUSSION

In the first stage of the study, a sample of the complex was subjected to complete stepwise sublimation at three different temperatures, 470, 500, and 530 K, on a VUP-5 vacuum setup at the residual pressure $p = 1.3 \times 10^{-3}$ Pa. Then the three samples obtained in this way were analyzed for C,H,N contents. It can be seen from Table 1, which summarizes the results of analysis, that all samples have the same composition corresponding to $CdPiv_2Phen$, i.e., the obtained result unambiguously corresponds to the congruent sublimation of the complex according to either or both of the two reactions

$$Cd_2Piv_4Phen_2\,(s.) = 2CdPiv_2Phen\,(gas), \quad (1)$$

$$Cd_2Piv_4Phen_2\,(s.) = 2CdPiv_2\,(gas) + 2Phen\,(gas) \quad (2)$$

provided that $p_{CdPiv_2} = p_{Phen}$.

Table 2. Major ion peak intensities in the mass spectrum of $Cd_2Piv_4Phen_2$ (T = 510 K, U_{ioniz} = 60 V)

m/z	Ion	Relative intensity, %
57	$(CH_3)_3C^+$	3
64	CdO^+	5
180	$Phen^+$	100
215	$CdPiv^+$	2
294	$CdPhen^+$	10
395	$CdPivPhen^+$	23
739	$[Cd_2Piv_3Phen + 28D]^+$	1.5

The thermodynamics and mechanism of vaporization of the cadmium phenanthroline complex were studied by the Knudsen effusion method with mass spectral analysis of the gas phase on an MC 1301 instrument in the temperature range of 450–520 K. Molybdenum Knudsen cells were used, with the ratio of evaporation area to effusion area being ~600. The temperature was measured by a Pt/Pt-Rh thermcouple and maintained to an accuracy of ±1°. The intensities of major peaks (relative to the ^{114}Cd isotope) recorded in the mass spectrum of the saturated vapor are summarized in Table 2.

Analysis of the mass spectrum provides the conclusion that complex-ligand molecules, being responsible for generation of the $CdPivPhen^+$ and $[Cd_2Piv_3Phen + 28D]^+$ ions, are present in the gas-phase of $Cd_2Piv_4Phen_2$.

For determining the molecular composition of the gas phase, the absolute partial pressures, and the character of congruent sublimation of cadmium pivalate phenanthroline complex, we experimentally studied the dissociative ionization of saturated vapor molecules and complete isothermal vaporization of a known weighed sample of the cadmium complex. Analysis of the ionization efficiency curves (IECs) and the appearance energies (*EA*) of the major ions present in the mass spectrum, $Phen^+$ (*EA* > 12.5 eV), $CdPhen^+$ (*EA* > 17.4 eV), $CdPivPhen^+$ (*EA* > 15.6 eV), showed that all ions are fragment ions formed upon the most probable dissociative ionization pathways of $CdPiv_2Phen$ molecules:

$$CdPiv_2Phen + \bar{e} \rightarrow CdPivPhen^+ + Piv^{\bullet} + 2\bar{e}, \quad (3)$$

$$CdPiv_2Phen + \bar{e} \rightarrow CdPhen^+ + 2Piv^{\bullet} + 2\bar{e}, \quad (4)$$

$$CdPiv_2Phen + \bar{e} \rightarrow Phen^+ + CdPiv_2 + 2\bar{e}. \quad (5)$$

The $[Cd_2Piv_3Phen + 28D]^+$ ion is probably generated from the $Cd_2Piv_4Phen_2$ dimer.

Thus, the saturated vapor over the cadmium pivalate phenanthroline complex consists almost entirely

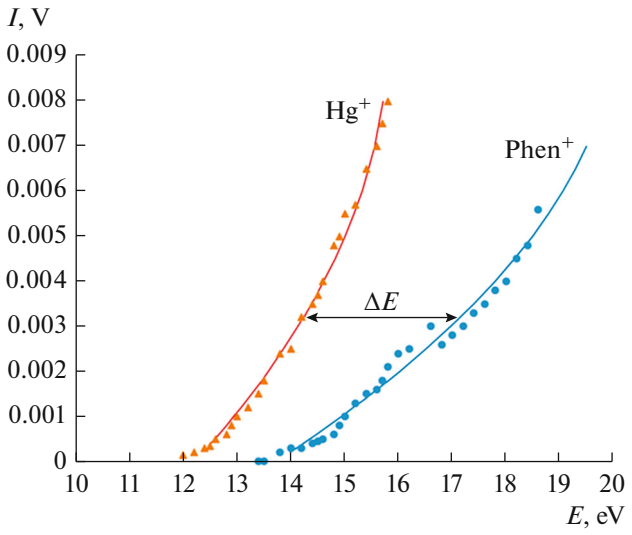

Fig. 1. Ionization efficiency curves for the phenanthroline $Phen^+$ ions and the Hg^+ standard.

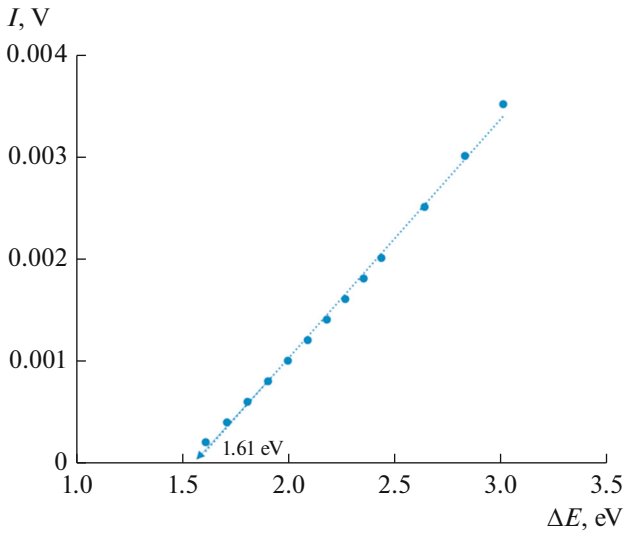

Fig. 2. The extrapolated voltage difference $\Delta E = f(I)$.

of monomeric $CdPiv_2Phen$ molecules and a minor amount of $Cd_2Piv_4Phen_2$ dimers. The vaporization can be described by two simple reactions (1) and (6):

$$Cd_2Piv_4Phen_2\,(s.) = Cd_2Piv_4Phen_2\,(gas). \qquad (6)$$

The experimental IECs for $Phen^+$ and Hg^+ ions (ionization energy (EI) = 10.41 eV) [12] (Fig. 1), processed by the extrapolated difference technique proposed by Warren [13] (Fig. 2), were used to determine the appearance energy of the phenanthroline ion: $EA_{Phen^+/CdPiv_2Phen} = 11.2 \pm 0.6$ eV. Using the $Phen^+$ appearance energy, phenanthroline ionization energy $EI_{Phen^+/Phen} = 8.51 \pm 0.02$ eV [12], and equation (7),

$$EA_{Phen^+/CdPiv_2Phen} \geq D_o^\circ + EI_{Phen^+/Phen}, \qquad (7)$$

we calculated the energy of dissociation $\left(D_o^\circ\right)$ (enthalpy ΔH_o°) of $CdPiv_2Phen$ molecule by the reaction

$$CdPiv_2Phen(gas) = CdPiv_2\,(gas) + Phen(gas). \qquad (8)$$

The enthalpy found in this way was $\Delta H_o^\circ \leq 260$ kJ/mol (2.69 eV). Here it must be noted that, since approximation (7) was used, the calculated value is the upper limit of the bond energy (enthalpy ΔH_o°) of phenanthroline and cadmium pivalate molecules.

As noted above, experiments on the complete isothermal sublimation of known weighed samples of $Cd_2Piv_4Phen_2$ were carried out to determine the character of vaporization and calculate the absolute partial pressures. The results of one of several experiments are shown in Fig. 3. The invariable ion current intensities throughout the period of sublimation and the absence of a non-volatile residue in the effusion cell at the end of the experiment confirm once again our conclusion about the congruent sublimation of the complex. The virtually single-molecule composition of the gas phase and experiments on complete isothermal sublimation of $Cd_2Piv_4Phen_2$ made it possible to use the Hertz–Knudsen equation

$$q_{Cd_2Piv_4Phen_2} = S_{eff}(M_{CdPiv_2Phen}/2\pi RT)^{1/2} p_{CdPiv_2Phen} t, \qquad (9)$$

where S_{eff} is the effective effusion area, M_{CdPiv_2Phen} is the molecular weight of the gas phase component, p_{CdPiv_2Phen} is the partial pressure of the gas phase component, t is the time of sublimation of a cadmium phenanthroline complex sample $q_{Cd_2Piv_4Phen_2}$, to calculate the partial pressure of the $CdPiv_2Phen$ molecules. The p value at $T = 493$ K found in this way was 2.37×10^{-1} Pa.

By investigating the temperature dependences of the ion currents I_{Phen^+}, I_{CdPhen^+}, $I_{CdPivPhen^+}$ the enthalpy of sublimation of the cadmium complex was calculated using the Clausius–Clapeyron equation by the least squares method (Table 3). This is exemplified in Fig. 4, which shows the experimental temperature dependence of the $CdPivPhen^+$ ion current. The enthalpies found using different ions are in good agreement with one another, which confirms our conclusion about $CdPiv_2Phen$ as the single molecular source for their origin.

The recommended value for the sublimation enthalpy of the cadmium phenanthroline complex $\Delta_S H_{298}^\circ = 186.9 \pm 4.6$ kJ/mol was found as the arithmetic mean over 14 independent measurements (Table 3).

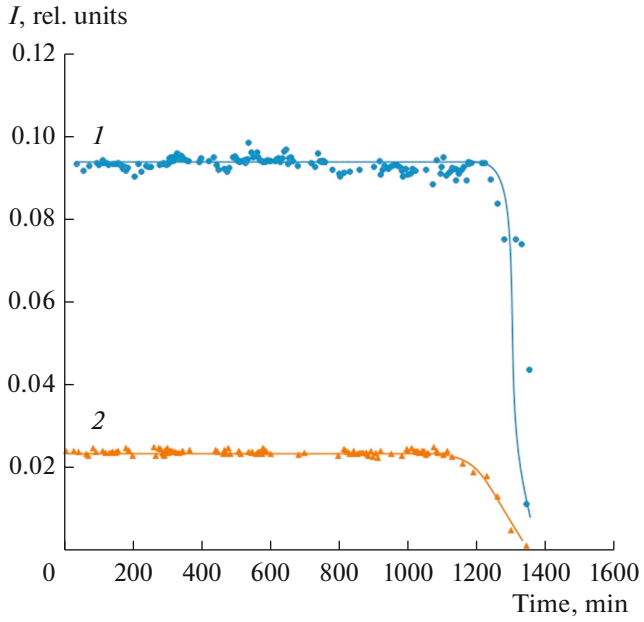

Fig. 3. Complete sublimation isotherm for the $Cd_2Piv_4Phen_2$ sample: $Phen^+$ ion current (*1*); $CdPivPhen^+$ ion current (*2*). $T = 493$ K.

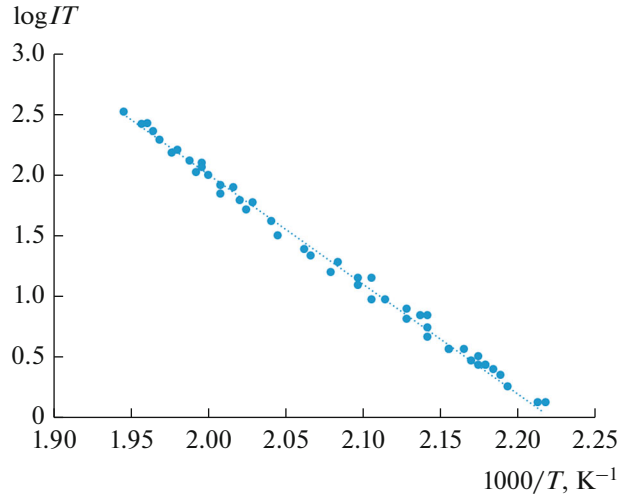

Fig. 4. Temperature dependence of $CdPivPhen^+$ ion current intensity.

Using the absolute partial pressure at $T = 493$ K and the enthalpy of sublimation of the cadmium complex, the equation for the temperature dependence of pressure (Pa) for the $CdPiv_2Phen$ molecules was derived:

$$\log p_{CdPiv_2Phen} = -(9760 \pm 240)/T + 19.17 \pm 0.15, \quad 450 \le T \le 520K. \qquad (10)$$

The absolute partial pressure of $CdPiv_2Phen$ allowed us to estimate the lower limit for the enthalpy of reaction (8) at $T = 500$ K using the third law of thermodynamics. The equilibrium constant for the reaction needed for this purpose $K_{eq} = 1.29 \times 10^{-6}$ Pa ($T = 500$ K) was found from the experimental value of the $CdPiv_2Phen$ partial pressure ($p_{CdPiv_2Phen} = 0.45$ Pa) and the partial pressures of cadmium pivalate and phenanthroline, $p_{Phen} = p_{CdPiv_2} = 7.5 \times 10^{-4}$ Pa, which are equal to the lower limit of sensitivity of the mass spectrometer. The value $\Delta_r S^0 = 146.4$ J/mol K used in the calculations corresponds to the entropies of gas-phase reactions with the change in the number of moles equal to unity. The enthalpy found for reaction (8) was $\Delta H^\circ_{500} = 177.5$ kJ/mol. Thus, the enthalpy of this reaction can be represented as $177.5 \le \Delta H^\circ_{500} \le 260$ kJ/mol.

Table 3. Enthalpies of sublimation of $CdPiv_2Phen$ in the 450–520 K range (kJ/mol)

$\Delta_s H^\circ_T$		
$Phen^+$	$CdPhen^+$	$CdPivPhen^+$
186.7 ± 4.9	190.9 ± 8.3	189.7 ± 6.7
180.6 ± 2.0	191.2 ± 4.1	186.9 ± 3.0
186.6 ± 3.5	180.9 ± 4.1	192.2 ± 3.3
179.5 ± 2.6	190.5 ± 3.7	192.8 ± 4.4
185.2 ± 2.7	182.2 ± 9.8	
Arithmetic mean		
183.7 ± 3.4	187.1 ± 5.1	190.4 ± 2.7

It is possible to consider what ratios of thermodynamic characteristics of the different ligand complex would ensure stability of the complex upon vaporization.

The vaporization of complexes ML_nL' can be either congruent [14],

$$AgPiv \cdot P(n\text{-}Bu)_3\,(s.) = AgPiv \cdot P(n\text{-}Bu)_3(gas), \qquad (11)$$

or incongruent where only one component predominantly passes to the gas phase, for example [9]:

$$[Ln(2,3,4\text{-}Tmoba)_3Phen]_2\,(s.) = Ln_2(2,3,4\text{-}Tmoba)_6\,(s.) + 2Phen(gas), \qquad (12)$$

where 2,3,4-Tmoba is 2,3,4-trimethoxybenzoate.

If the enthalpy of incongruent vaporization of the complex

$$ML_nL'(s.) = ML_n(s.) + L'(gas) \qquad (13)$$

is higher than the enthalpy of sublimation

$$ML_nL'(s.) = ML_nL'(gas), \qquad (14)$$

while the enthalpy of dissociation of this complex in the gas phase

$$ML_nL'(gas) = ML_n(gas) + L'(gas) \qquad (15)$$

is commensurable with or somewhat higher than the enthalpy of sublimation, then the gas phase is likely to contain different-ligand complexes. In view of the above, the enthalpy of thermal decomposition of the cadmium complex by the reaction

$$CdPiv_2Phen(s.) = CdPiv_2(s.) + Phen(gas) \quad (16)$$

should be greater than the enthalpy of reaction (8).

In conclusion, it can be noted that thermodynamic characteristics of cadmium phenanthroline complex make it suitable as a precursor for CVD production of oxide coatings or nanocrystalline films.

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