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Vapour pressures and standard molar enthalpies of sublimation of beryllium(II) and aluminium(III) benzoylacetonates

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Abstract

The simultaneous torsion and mass-loss effusion technique was used to measure the vapour pressure of crystalline bis(benzoylacetonato)beryllium(II) – $Be(BZAC)_2$ – and tris(benzoylacetonato)aluminium(III) – $Al(BZAC)_3$ – , as a function of temperature, from 415.7 K to 437.6 K and from 461.9 K to 478.2 K respectively. From the temperature dependence of the vapour pressure, the standard molar enthalpies of sublimation, at the mean temperature of the experimental temperature ranges, were derived for both complexes. The mean values obtained from both techniques are: $Be(BZAC)_2$, $\Delta_{cr}^{g}H_{m}^{\circ}(426.6\ \mathrm{K}) = 151.6 \pm 1.8\ \mathrm{kJ\ mol^{-1}}$; $Al(BZAC)_3$, $\Delta_{cr}^{g}H_{m}^{\circ}(470.1\ \mathrm{K}) = 186.6 \pm 2.1\ \mathrm{kJ\ mol^{-1}}$. Using the estimated value of $\Delta_{cr}^{g}C_{p}^{\circ} = -50\ \mathrm{J\ K^{-1}\ mol^{-1}}$, for both beryllium(II) and aluminium(III) complexes, the standard molar enthalpies of sublimation at 298.15 K, were calculated as $158.0 \pm 1.8\ \mathrm{kJ\ mol^{-1}}$ and $195.2 \pm 2.1\ \mathrm{kJ\ mol^{-1}}$ respectively.

Keywords: Vapour pressures; Enthalpy of sublimation; Bis(benzoylacetonato)beryllium(II); Tris(benzoylacetonato)aluminium(III)

1. Introduction

Standard molar enthalpies of sublimation of metal complexes are key values for the calculation of the mean bond dissociation enthalpies between the metal and the ligands, and hence for a better understanding of the energetics of the chemical bonds on these compounds.

In a previous work [1] we reported the standard molar enthalpies of sublimation of seven crystalline copper(II) β-diketonates using both torsion and knudsen mass loss effusion techniques. Comparing those results with the vacuum drop sublimation microcalorimetric values, for the same complexes, reported before [2], we found that the effusion results are about 5 kJ mol^{-1} higher. In this paper we report results for the vapour pressures and standard molar enthalpies of sublimation of two crystalline metal benzoylacetonates (benzoylacetone is 1-phenylbutane-1,3-dione). The results obtained for the enthalpies of sublimation in this work are compared with previously reported vacuum sublimation microcalorimetric values [3].

2. Experimental details

The metal complexes, bis(benzoylacetonato)beryllium(II) – $Be(BZAC)_2$ – and tris(benzoylacetonato)aluminium(III) – $Al(BZAC)_3$ – were prepared as described before [3] and twice sublimed in vacuum. The analysis of the compounds obtained is presented in Table 1.

The apparatus and the technique have been described in detail elsewhere [4]. The principal features were as follows: a cylindrical cell, containing the crystalline sample, was suspended from a vacuum microbalance by two phosphor-bronze torsion bands 1 mm apart. The cell was provided with two effusion holes, of 1 mm diameter, made of 6 μm platinum foil and positioned 20 mm apart on opposite sides of the cell. The temperature of the sample was measured by a thermistor placed inside the cell. The measuring procedure was completely automatic and controlled by a desktop computer. The following quantities, read by a voltmeter, were input to the computer: the temperature, the current I (required to compensate electromagnetically the recoil force of the effusing molecules), and the mass loss from the effusion cell. The voltmeter readings were repeated five times and the average stored in the computer together with elapsed time. This procedure was repeated six times at 30 s intervals. From the measured quantities two values of vapour pressure were obtained:

(1) the mass loss pressure p_m, derived by Eq. (1), where w_0 is taken as unity

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Table 1
Analysis (mass%) of the metal complexes $Be(BZAC)_2$ and $Al(BZAC)_3$

Complex	C	H	Metal	C	H	Metal
		(found)			(expected)	
$Be(BZAC)_2$	72.69	5.46	2.68	72.47	5.48	2.72
$Al(BZAC)_3$	70.43	5.34	5.28	70.58	5.33	5.28

Table 2
Experimental results for the studied complexes

Complex	Measurement	T_1/K	T_2/K	$\langle T\rangle$/K	a	b	$\Delta^g_{cr}H^\circ_m(\langle T\rangle)$ (kJ mol^{-1})	$\Delta^g_{cr}H^\circ_m$(298.15 K) (kJ mol^{-1})	$\frac{p_m}{p_t}(\langle T\rangle)$
$Be(BZAC)_2$	Torsion	415.7	437.6	426.6	41.475±0.589	18210±253	151.4±2.1	157.8±2.1	1.01
	Mass-loss	415.7	437.6	426.6	41.568±0.785	18246±337	151.7±2.8	158.1±2.8	
	Mean						151.6±1.8	158.0±1.8	
$Al(BZAC)_3$	Torsion	461.9	478.2	470.1	46.491±0.875	22348±409	185.8±3.4	194.4±3.4	1.02
	Mass-loss	461.9	478.2	470.1	46.916±0.669	22540±313	187.4±2.6	196.0±2.6	
	Mean						186.6±2.1	195.2±2.1	

Table 3
(T,p) mean values from the vapour pressure equations

p/Pa	T/K	
	$Be(BZAC)_2$	$Al(BZAC)_3$
0.1	415.9	458.0
0.2	422.6	464.6
0.3	426.6	468.5
0.4	429.5	471.3
0.5	431.8	473.5
0.6	433.7	475.4
0.7	435.3	476.9
0.8	436.6	478.3
0.9	437.9	479.5
1.0	439.0	480.6

Table 4
Standard molar enthalpies of sublimation for the studied complexes

Complex	$\Delta^g_{cr}H^\circ_m$(298.15 K)/kJ mol^{-1}	
	Present work	Calorimetric (Ref. [3])
$Be(BZAC)_2$	158.0±1.8	142.3±1.4
$Al(BZAC)_3$	195.2±2.1	193.7±0.3

$$p_m = (\Delta m/A_0 w_0 t)(2\pi R T/M)^{1/2} \qquad (1)$$

in which Δm is the sublimed mass during the effusion time period, t, A_0 is the area of the effusion hole, M is the molar mass of the effusing vapour and R is the gas constant.

(2) the torsion pressure p_t, calculated according to $p_t = cI$, where c is a constant of the apparatus obtained by calibration with naphthalene.

Within a period of approximately 180 s, five sets of values for p_m, p_t and T were obtained. The first series of values stored were for $p \approx 0.08$ Pa and then the temperature of the oven surrounding the effusion cell was automatically increased, so the temperature of the cell would be about 0.9 K higher. After allowing for the temperature in the cell to be constant, measurements were repeated as described above. The sequence was stopped when the vapour pressure exceeded 1.2 Pa. During the effusion process the vacuum outside the cell was less than 10^{-3} Pa and before a new run started the temperature of the oven was lowered to its initial value. After four or five runs the cell was turned 180° around its horizontal axis, in order to reverse the effusion torque during the subsequent runs. Measurements with right and left turn sense of the effusion torque allowed elimination of any small systematic error in the torsion effusion measurement. Eventual processes of decomposition, dissociation or association of the sample molecules, in the vapour phase, could be detected because then the ratio p_m/p_t would be significantly different from unity [5].

3. Results and discussion

The Clausius–Clapeyron equation, $\ln(p/\text{Pa}) = a - b$ k/T, where $b = \Delta^g_{cr}H^\circ_m\langle T\rangle/\text{R}$, was used to derive the standard molar enthalpies of sublimation at the mean temperature $\langle T\rangle$ of the experimental temperature range, for both the mass-loss and torsion effusion results (mean of at least five runs). Table 2 presents the results for the studied complexes: the mean temperature $\langle T\rangle$ of the experiments, the parameters of the Clausius–Clapeyron equation, the standard molar enthalpy of sublimation $\Delta_{cr}^{g}H_{m}^{o}$ at temperature $T=\langle T\rangle$ and the values of the ratios p_m/p_t calculated for each complex at the mean temperature $\langle T\rangle$; the standard molar enthalpy of sublimation at $T=298.15$ K is also presented. This value was derived from the value of the sublimation enthalpy calculated at the mean temperature $\langle T\rangle$ by the equation:

$$\Delta_{cr}^{g}H_{m}^{o}(298.15\text{ K}) = \Delta_{cr}^{g}H_{m}^{o}\langle T\rangle + \Delta_{cr}^{g}C_{p,m}^{o}(298.15\text{ K}-\langle T\rangle) \quad (2)$$

Since there are no published values of $\Delta_{cr}^{g}C_{p,m}^{o}$ for the studied complexes, we assumed $\Delta_{cr}^{g}C_{p,m}^{o}=-50$ J K^{-1} mol^{-1} in our calculations in accordance with estimations made by other authors [6] and with the procedure that we have followed, in previous works, for some β-diketones [7] and copper β-diketonates [1].

There is an excellent agreement between the results obtained from mass-loss and from torsion measurements. The ratios p_m/p_t calculated at the mean temperature $\langle T\rangle$ are nearly unity, indicating that there was no decomposition, dissociation or association of the complexes' molecules in the vapour phase.

Table 3 lists, for both studied complexes, the pressure–temperature mean values obtained from the vapour pressure equations over the experimental vapour pressure range 0.1–1.0 Pa. Table 4 compares the present results of the standard molar enthalpies of sublimation, at 298.15 K, with literature values obtained by microcalorimetry using the sublimation vacuum drop technique [3]. For $Al(BZAC)_3$, there is an excellent agreement between the results obtained both from the vapour pressures and from the microcalorimetric methods, but for $Be(BZAC)_2$, the values derived from both methods are some 16 kJ mol^{-1} apart. There is no way to explain this discrepancy, but at the present the value derived from the vapour pressures method seems to be more reliable since it is obtained from two different experimental methods.

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