

THERMODYNAMIC STUDY OF A SERIES LITHIUM β -DIKETONATES

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Thermal behaviour of a series of lithium β -diketonates: Li(dpm) (*dpm*=dipivaloylmethanate (2,2,6,6-tetramethylheptane-3,5-dione)), Li(pta) (*pta*=pivaloyltrifluoroacetate (2,2-dimethyl-6,6,6-trifluoro-3,5-hexanedione)), Li(tfa) (*tfa*=trifluoroacetylacetate (1,1,1-trifluoro-2,4-pentandione)), Li(hfa) (*hfa*=hexafluoroacetylacetate (1,1,1,5,5,5-hexafluoro-2,4-pentandione)) has been investigated. Gas phase composition of these complexes has been established. Temperature dependences of vapor pressure of lithium compounds were obtained by static and dynamic methods, and thermodynamic parameters were calculated. Dependence of compound volatility on ligand structure is shown. For Li(dpm) detailed investigation has been done by differential scanning calorimetry (DSC).

Keywords: β -diketonates, DSC, DTA, lithium, thermodynamic parameters, vapour pressure

Introduction

Due to their thermal properties, especially volatility, metal β -diketonates find a wide application in technology e.g. gas chromatography and as precursors in chemical vapor deposition of metal and oxide coatings [1–4]. For many metal β -diketonates, basic factors governing the thermal properties such as volatility and stability have been revealed. However β -diketonates of alkali metals and especially lithium, the smallest, most polarizing alkali metal, have been paid less attention. There is a number of works describing synthesis of some lithium β -diketonates [5–8], but their thermal properties did not studied. Thermoanalytical study is carried out only for sodium and potassium dipivaloylmethanates [8]. There is the only work on lithium complexes where thermodynamic parameters for Li(dpm) are calculated from temperature dependence of vapour pressure [9] obtained by effusion Knudsen method with mass recording in the temperature 180–250°C: $\Delta_{\text{subl}} H_{\text{T}}^0 = 174.4 \text{ kJ mol}^{-1}$ and $\Delta_{\text{subl}} S_{\text{T}}^0 = 293.3 \text{ J K}^{-1} \text{ mol}^{-1}$. However, calculations have been done with the assumption that the complex is monomeric in the absence of accurate data on compound composition in gas phase.

Thus, the aim of this paper is to obtain reliable data on the temperature dependence of saturated vapour pressure and calculation of thermodynamic parameters taking into consideration the experimental data on gas phase composition.

Experimental

The complexes were synthesized by the interaction of lithium hydroxide monohydrate with the appropriate

β -diketone as described in [7]. Compounds were purified by gradient sublimation at $P=1 \text{ Pa}$ and temperature 453–493 K. Yield of pure compounds was 70–80%. Compounds were characterized by CHF elemental analysis at Carlo-Erba 1106 (Italy) device. Anal. found/calc. (%) for Li(pta) ($\text{C}_8\text{H}_{10}\text{O}_2\text{F}_3\text{Li}$): C, 47.6/47.5, H, 5.1/5.0, F, 26.7/28.2; Li(hfa) ($\text{C}_5\text{HO}_2\text{F}_6\text{Li}$): C, 27.4/28.1, H, 0.8/0.5, F, 52.3/53.3; Li(tfa) ($\text{C}_5\text{H}_4\text{O}_2\text{F}_3\text{Li}$): C, 36.9/37.5, H, 2.4/2.5, F, 34.2/35.6; Li(dpm) ($\text{C}_{11}\text{H}_{19}\text{O}_2\text{Li}$): C, 69.8/69.5, H, 9.5/10.1. While synthesized compounds readily hydrolyzed in air, they are stored well in desiccator.

DTA experiments were carried out with Q-1500-D (MOM, Hungary) device at a linear heating rate 5 K min^{-1} in ceramic micro-pots in He. The samples were 40–50 mg and the maximum error of measurements (Δt°) was 5 K.

DSC experiments were performed with Setaram DSC 111 device at heating rate $1\text{--}3 \text{ K min}^{-1}$ using standard technique. The samples of 20–30 mg were placed in the evacuated glass ampoules. Limiting error of measured thermo effects was 2%. Calorimetry measurements were carried out at temperature range 528–573 K.

Electron impact mass spectra were recorded by MX-1310 (USSR) mass spectrometer with direct probe insertion. Electron energy was 70 eV.

The saturated vapour pressure above solid phase of the reported complexes has been measured by flow method using He as gas-carrier. Experimental technique is described in [10]. Amount of He (error in measuring the flow rate is $\pm 2\%$) was passed through the solid compound at the given temperature ($\pm 0.5 \text{ K}$). The compound is converted from the solid into the gas state

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and deposited in the cool zone. The quantity of the compound converted into gas state is determined by weighing ($\pm 5 \cdot 10^{-4}$ g). Design of the experimental setup enables to avoid the contribution of diffusion and edge effects. The experiments were carried out at quasi-equilibrium conditions of vaporization i.e. carrier gas was saturated by the studied compound vapours and diffusion was negligible. That is confirmed by the fact that the measured values of vapour pressure of the studied compounds are not affected by flow rate of the carrier gas (from 0.5 to 2 L h⁻¹) in all temperature range. Statistical precision of the technique is not more than $\pm 10\%$.

For Li(dpm), measurement of vapour pressure have been also carried out by static method with a quartz membrane zero manometer [11]. During the experiments the zero manometer was thermostated. The temperature of the sample was maintained within ± 0.1 K throughout the temperature range employed in this study. Detailed description of experimental technique is given in [11]. In the used technique the pressure and temperature measurement error did not exceed ± 40 Pa and ± 0.25 K.

Results and discussion

In the mass spectrum of Li(hfa), Li(tfa), Li(pta) ion peak with maximal mass corresponds to $[\text{Li}_2(\text{hfa})_2]^+$, $[\text{Li}_2(\text{tfa})_2]^+$ and $[\text{Li}_2(\text{pta})_2]^+$ respectively that indicates to dimeric structure of these compounds. In a similar manner, Li(dpm) has a tetrameric structure. Note, lithium pivaloylacetate [12] and acetylacetate [13] complexes have polymeric structure in solid-state that seems to be typical for lithium β -diketonate complexes.

From the solid residue amount (14, 4, 14 and 11% for Li(dpm), Li(pta), Li(tfa) and Li(hfa), respectively) calculated from thermogravimetric curves in Fig. 1, one can say that only Li(pta) has noticeable volatility

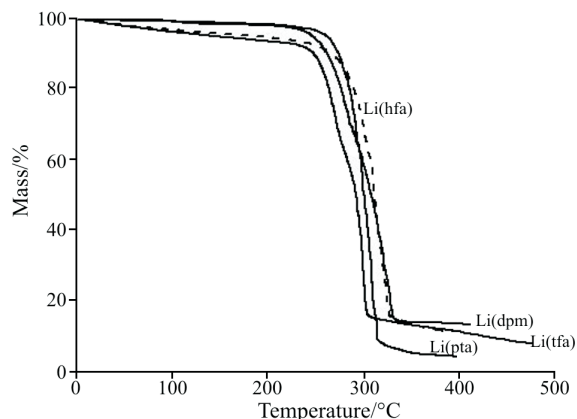


Fig. 1 TG curves for lithium β -diketonates

because residue amount is essentially less than theoretically possible (converting into LiF). Other complexes in this series decompose mainly.

Figure 2 and Table 1 show temperature dependences of vapour pressure obtained by flow and static methods and vapourization thermodynamic parameters for studied complexes. The calculation of vapour pressure has been done taking into account the composition of gas phase established from mass spectra. Based on tensimetric data the following volatility row was suggested: $\text{Li(pta)} > \text{Li(dpm)} > \text{Li(hfa)} > \text{Li(tfa)}$. The same tendency is known for alkali earth metal β -diketonates [14]. Table 1 shows that Li(tfa) and Li(hfa) have close values of ΔH and vapour pressure, while for Li(pta) and Li(dpm) values of ΔH are close but there is a noticeable difference in vapour pressure. Thus we can suppose that entropy (i.e. degree of disordering upon phase transition) makes the main contribution into difference of volatility of these compounds.

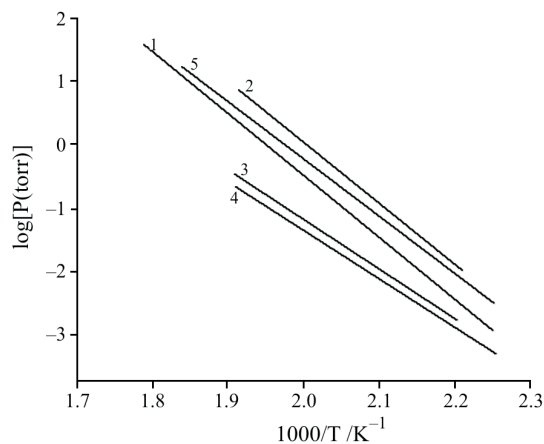


Fig. 2 Temperature dependences of the saturated vapour pressure for lithium β -diketonates: 1 – $^{\circ}\text{[Li(dpm)]}_4$, 2 – Li(pta), 3 – Li(hfa), 4 – Li(tfa), 5 – $^{\text{b}}\text{[Li(dpm)]}_4$

Taking into account that for Li(dpm) some literature data [9] are available we carried out more detailed study for this complex.

Figure 3 shows unsaturated and saturated vapour pressure data of Li(dpm) obtained by flow and static methods over solid and by static over liquid. Data obtained by these two methods are in a good agreement.

The average molecular mass was calculated for Li(dpm) in gas phase from data on unsaturated vapour pressure obtained by static method (Table 2). Found values for molecular mass are close to calculated value 759.8 for $[\text{Li(dpm)}]_4$. These data are in an agreement with obtained mass spectrometric data on compounds composition.

Thermal behaviour of Li(dpm) was studied by DSC in the temperature range 528–573 K. In this temperature range only one phase conversion – melting of compound has been observed. Melting point of the

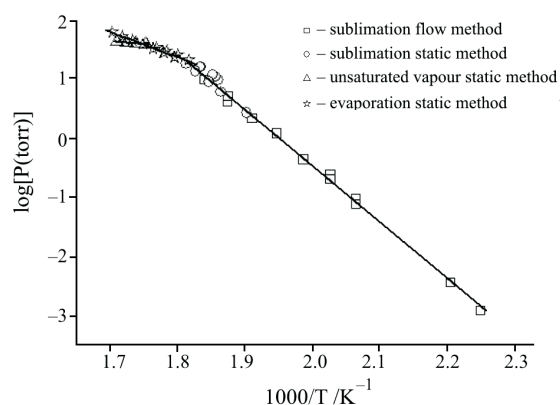
Table 1 Thermodynamic parameters for sublimation of lithium β -diketonates

Compound	Method	Number of points	$\lg P(\text{torr})=A-B/T/\text{K}^{-1}$		$\Delta H_{\text{T}}^0/\text{kJ mol}^{-1}$	$\Delta S_{\text{T}}^0/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta T/\text{K}$
			A	B			
[Li(dpm)] ₄	flow	13	18.5	9480	181.1±2.8	298.2±5.6	444–543
[Li(dpm)] ₄	static	10	20.1	10366	198.0±15.1	329.4±27.8	537–545
[Li(dpm)] ₄	^c flow/static	23	18.2	9312	178.3±2.0	292.5±3.9	444–549
^a [Li(dpm)] ₄	static	17	10.3	4995	95.6±1.3	142.1±2.3	550–581
^b [Li(dpm)] ₄	Knudsen	12	18.0	9112	174.3±8.5	289.5±14.5	453–523
[Li(pta)] ₂	flow	12	19.1	9526	182.0±2.3	309.3±4.6	453–523
[Li(tfa)] ₂	flow	7	13.9	7620	145.6±3.0	210.7±6.3	443–523
[Li(hfa)] ₂	flow	13	14.5	7826	149.5±3.5	221.5±7.0	453–523

^aevaporation, ^brefined data from [9]; ^cco-processing data obtained by flow and static methods

Table 2 Molecular masses for [Li(dpm)]₄ ($M_{\text{calc}}=759.8$) in gas phase calculated from unsaturated vapour pressure data

T/K	P/torr	$M_{\text{found}}/\text{g mol}^{-1}$	$\Delta M/M_{\text{calc}}/\%$
570.29	36.39	753	0.8
575.24	37.82	730	3.8
580.11	39.2	711	6.4
584.99	40.3	698	8.1

**Fig. 3** Temperature dependence of the saturated and unsaturated vapour pressure for Li(dpm)

compound is 549 ± 1 K. Thermodynamic parameters are the following: $\Delta_{\text{melt}} H_{549}^0 = 82.4 \pm 1.6$ kJ mol⁻¹, $\Delta_{\text{melt}} S_{549}^0 = 148.6 \pm 3.8$ J mol⁻¹ K⁻¹ (calculations were made for tetramer).

The same thermodynamic parameters for melting process of Li(dpm) calculated from the data of sublimation and evaporation processes are the following: $T_{\text{melt}} = 549.4$ K, $\Delta_{\text{melt}} H_{549.4}^0 = 82.7 \pm 2.4$ kJ mol⁻¹, $\Delta_{\text{melt}} S_{549.4}^0 = 150.4 \pm 4.5$ J mol⁻¹ K⁻¹ and data are in an agreement with that obtained by DSC within the experiment error.

In summary, dependence of compound volatility on ligand structure is shown from the investigation of thermal properties of a series of lithium β -diketonates. Evaporation thermodynamic parameters have been calculated.

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