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DSC DETERMINATION OF THE FUSION AND SUBLIMATION ENTHALPY OF BIS(2,4-PENTANEDIONATO)BERYLLIUM(II) AND TRIS(2,4-PENTANEDIONATO)ALUMINIUM(III)

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ABSTRACT

The sublimation enthalpy of bis(2,4-pentanedionato)beryllium(II) and of tris(2,4-pentanedionato)aluminium(III) has been determined by differential scanning calorimetry as 85.3 ± 3.5 kJ mole^{-1} and 125.6 ± 3.2 kJ mole^{-1}, respectively. The corresponding fusion enthalpies are 15.67 ± 0.74 and 28.71 ± 1.34 kJ mole^{-1}, respectively.

INTRODUCTION

Sublimation enthalpies of metal complexes are essential prerequisite data for the calculation of metal–ligand thermochemical bond energies. The sublimation enthalpy of bis(2,4-pentanedionato)beryllium(II) has been determined by Berg and Truemper [1,2] as 35.61 kJ mole^{-1} based on isoteniscopic vapour pressure/temperature data and by Naghibi [3] as 93.72 ± 2.09 kJ mole^{-1} using the Knudsen effusion method. Sachinidis and Hill [4] have reviewed the published sublimation enthalpy data for tris(2,4-pentanedionato)aluminium(III) and have selected $\Delta H_{\text{sub}}[\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3] = 118.6 \pm 7.8$ kJ mole^{-1}. Recently Teghil et al. [5] have determined the vapour pressure of tris(2,4-pentanedionato)aluminium(III) over the temperature range 337–405 K using the torsion effusion method and have reported the corresponding sublimation enthalpy as 47 ± 1 kJ mole^{-1} (298 K) which is considerably deviated from the range selected by Sachinidis and Hill [4].

This paper reports the sublimation enthalpy and fusion enthalpy of bis(2,4-pentanedionato)beryllium(II) and tris(2,4-pentanedionato)aluminium(III) as derived by differential scanning calorimetry. Metal–oxygen thermochemical bond energies are recalculated based on the most recent

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thermochemical data for these complexes. Also further relevant published thermochemical data for these and related complexes are critically reviewed.

EXPERIMENTAL

Bis(2,4-pentanedionato)beryllium(II) was prepared according to the method of Yoshida et al. [6] and recrystallised from methanol/water 50 : 50 v/v (m.p. 108; lit. 108°C [7]). Tris(2,4-pentanedionato)aluminium(III) was prepared by a published procedure [7] and purified by repeated sublimation (m.p. 194–195; lit. 194.6°C [7]). Microanalysis data (Amdel Australian Microanalytical Service, Australia) for these complexes are given in Table 1.

TG–DSC data were obtained using a Rigaku-Denki (Thermoflex 8085) simultaneous TG–DSC system. For thermal analysis in a dry nitrogen atmosphere, a gas flow rate of 0.1 dm^3 min^{-1} was employed and for vacuum DSC studies, the sample chamber pressure was maintained at 5×10^{-3} τ. Sample and alumina reference masses ranged from 3 to 10 mg and a heating rate of 5°C min^{-1} was employed, DSC sample preparation has been described in detail previously [8]. DSC peak areas were derived using an on-line Interdata 616 minicomputer via a bi-directional A/D converter and associated interface which allowed sampling at the rate of 10 readings/s. The data analysis procedure has been described previously [8]. Different calibrants were used for fusion and sublimation studies: indium, $\Delta H_{fus} = 3.29 \pm 0.01$ kJ $mole^{-1}$ and benzoic acid, $\Delta H_{sub} = 89.7 \pm 0.5$ kJ $mole^{-1}$, respectively [8]. The corresponding instrument constants are 0.758 and 0.672, respectively. The uncertainty intervals associated with derived enthalpy data are quoted as the standard deviation of the mean.

RESULTS AND DISCUSSION

Representative TG–DSC thermograms for bis(2,4-pentanedionato)beryllium(II) are shown in Figs. 1, 2 and 3. The TG–DSC data (Fig. 1) refer to

TABLE 1

Microanalysis data for Be(II) and Al(III) β-diketonate complexes

Complex	Calculated		Found	
	C	H	C	H
$Be(acac)_2$	57.96	6.81	57.47	6.72
$Al(acac)_3$	55.55	6.53	55.35	6.61

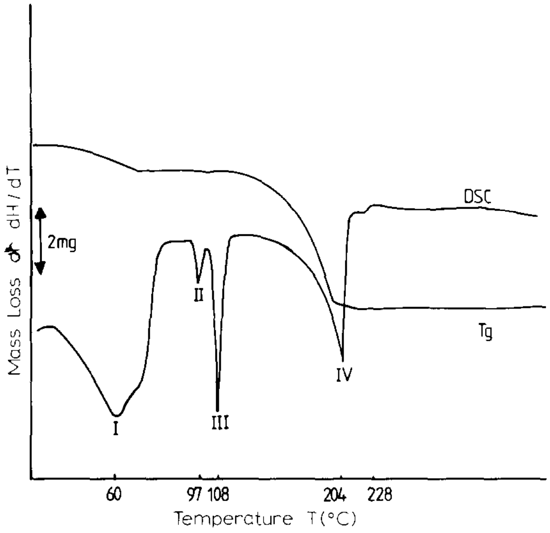

Fig. 1. Typical TG–DSC thermogram (nitrogen) of $Be(acac)_2$(hydrate). Sample mass, 5.22 mg; vaporisation temperature range, 120–228°C; vaporisation peak temperature, 204°C.

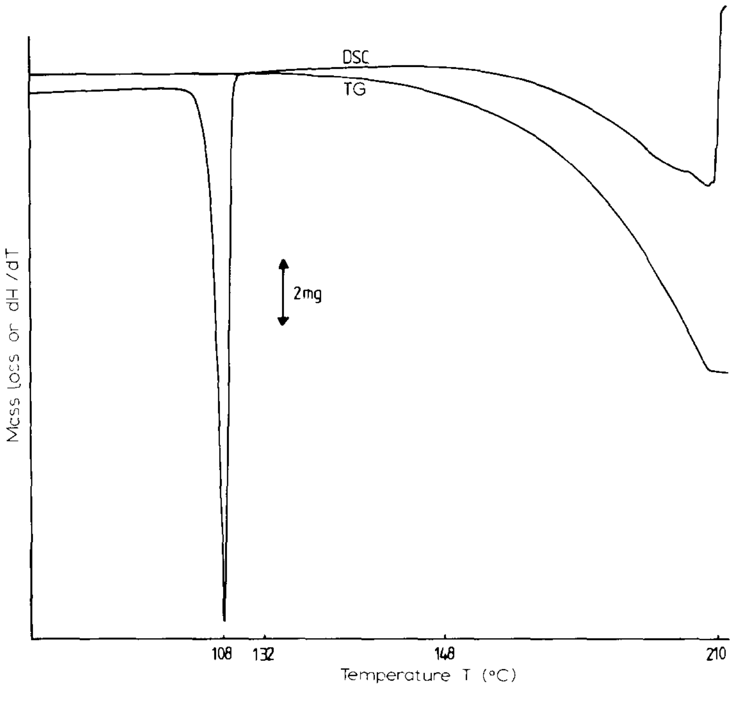

Fig. 2. Typical TG–DSC thermogram (nitrogen) of $Be(acac)_2$ (anhydrous). Sample mass, 9.94mg; vaporisation temperature range, 132–210°C.

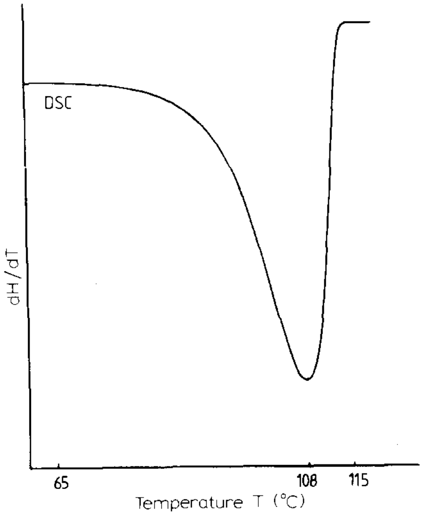

Fig. 3. Typical TG–DSC thermogram (vacuum) of Be(acac)$_2$. Sample mass, 6.84 mg; sublimation temperature range, 65–115°C; sublimation peak temperature, 108°C.

thermal analysis using a nitrogen atmosphere and to the hydrated complex. Four endotherms are indicated which may be assigned as I, dehydration; II, an irreversible solid-state phase change; III, fusion, and IV, vaporisation. Yoshida et al. [6] have previously reported a solid-state phase change for bis(2,4-pentanedionato)beryllium(II) at 97°C and the irreversible nature of this phase change is indicated by the absence of endotherm II in a TG–DSC thermogram of a sample preheated to 97°C, cooled and reheated (Fig. 2). For the anhydrous complex, smooth sublimation occurs over the temperature range 65–115°C (Fig. 3). The fusion enthalpy for bis(2,4-pentanedionato)beryllium(II) was derived from thermograms of the type shown in

TABLE 2

Fusion enthalpy of bis(2,4-pentanedionato)beryllium(II)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{fus} (kJ mole^{-1})
9.94	±4	16.48
9.92	±4	16.02
6.68	±4	16.57
6.98	±4	15.15
6.74	±4	15.48
6.72	±4	14.50
12.26	±8	15.52

$\Delta H_{\mathrm{fus}} = 15.67 \pm 0.74$ kJ mole^{-1}

TABLE 3

Sublimation enthalpy of bis(2,4-pentanedionato)beryllium(II)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{sub} (kJ $mole^{-1}$)
9.31	±4	86.7
8.17	±4	85.1
8.38	±4	80.8
8.19	±4	89.2
9.02	±4	88.2
5.53	±2	78.9
6.62	±2	86.4
6.31	±4	84.2
8.67	±4	88.9
7.38	±4	85.0
12.12	±8	89.4
10.18	±8	89.6
6.84	±4	86.9
7.77	±2	81.1
7.69	±2	79.8

$\Delta H_{sub} = 85.3 \pm 3.5$ kJ $mole^{-1}$

Fig. 2 and the corresponding sublimation enthalpy was derived from thermograms of the type shown in Fig. 3 and are summarised in Tables 2 and 3, respectively.

For tris(2,4-pentanedionato)aluminium(III), the DSC profiles, nitrogen and vacuum atmospheres, are similar to those for bis(2,4-pentanedionato)beryllium(II) (Figs. 2 and 3, respectively). Sublimation occurs over the temperature range 110–170°C and fusion occurs at 194.6°C. The derived fusion and sublimation enthalpy data for tris(2,4-

TABLE 4

Fusion enthalpy of tris(2,4-pentanedionato)aluminium(III)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{fus} (kJ $mole^{-1}$)
10.09	±8	30.36
13.11	±8	29.10
8.51	±4	28.88
8.47	±8	28.89
6.84	±4	26.25
11.05	±16	28.77

$\Delta H_{fus} = 28.71 \pm 1.34$ kJ $mole^{-1}$

TABLE 5

Sublimation enthalpy of tris (2,4-pentanedionato)aluminium(III)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{sub} (kJ $mole^{-1}$)
16.51	±8	126.4
11.22	±4	128.5
9.77	±4	126.7
8.21	±4	119.7
12.82	±8	128.7
10.89	±4	127.4
9.80	±4	124.4
10.11	±4	129.5
6.26	±4	126.6
7.17	±4	120.7
9.79	±4	130.6
7.14	±4	120.7
8.22	±4	125.5
7.39	±4	127.4
10.40	±4	127.0
8.22	±4	124.8
8.72	±4	121.1

$\Delta H_{sub} = 125.6 \pm 3.2$ kJ $mole^{-1}$

pentanedionato)aluminium(III) are summarised in Tables 4 and 5, respectively.

For bis(2,4-pentanedionato)beryllium(II), the DSC mean value of 85.3 kJ $mole^{-1}$ is close to that of Naghibi [3] and hence neglecting the isoteniscopic data of Berg and Truemper [1,2], $\Delta H_{sub}[Be(C_5H_7O_2)_2]$ is selected as 89.5 ± 2.88 kJ $mole^{-1}$ which represents the mean of the recent data.

For tris(2,4-pentanedionato)aluminium(III) the new DSC value for the sublimation enthalpy of this complex of 125.6 kJ $mole^{-1}$ is within the limits of the 'selected' value of Sachinidis and Hill [4] and thus no modification of this selected value is necessary.

The derivation of metal–oxygen thermochemical bond energies is based upon calculation of the enthalpy change associated with the gas phase formation reaction

$$M_{(g)} + nC_5H_7\dot{O}_{2(g)} \xrightarrow{\Delta H_{f_r}} M(C_5H_7O_2)_{n(g)}$$

It is known [9] that the metal–oxygen coordinate bond lengths are equal in these complexes and hence the homolytic metal–oxygen thermochemical bond energy, $\bar{D}$(M–O) = $\Delta H_{f_r}/2n$. Cavell and Pilcher [10] have calculated $\Delta H_f^0[C_5H_7\dot{O}_{2(g)}] = -235.7$ kJ $mole^{-1}$ based upon an estimated $\bar{D}$(O–H, enol) = 365 kJ $mole^{-1}$.

For bis(2,4-pentanedionato)beryllium(II), Irving and Riberio da Silva [11] report $\Delta H_f^0[\mathrm{Be(C_5H_7O_2)_2}]_{(c)}$ (298 K) = −1247.1 kJ mole^{-1} as derived by solution calorimetry. $\Delta H_f^0\mathrm{Be}_{(g)}$ = 324.3 kJ mole^{-1} [12] and thus $\bar{D}$(Be–O) = 253 kJ.

The enthalpy of combustion (298 K) of tris(2,4-pentanedionato)aluminium(III) has been determined by Cavell and Pilcher [10] as 7948.4 kJ mole^{-1} and $\Delta H_f^0[\mathrm{Al(C_5H_7O_2)_3}]_{(c)}$ = −1793.3 kJ mole^{-1}. $\Delta H_f^0\mathrm{Al}_{(g)}$ = 329.3 kJ mole^{-1} [13] and thus $\bar{D}$(Al–O) = 216 kJ.

The uncertainty associated with these thermochemical bond energies is large but trends in these data are realistic. Thus the beryllium–oxygen coordinate bond is significantly stronger than the aluminium–oxygen coordinate bond which is a reflection of the greater covalent character associated with the former due to the smaller cationic radius: Be(II), 41.0 pm; Al(III), 67.5 pm. [14].

It is relevant to briefly review other published thermochemical data relating to Be(II) and Al(III) β-diketonate complexes. Sublimation enthalpies of several Be(II) and Al(III) β-diketonate complexes have been determined by Berg and Truemper [1,2] using an isoteniscope to derive the relevant vapour pressure/temperature data. The data are reproduced in Table 6. Even though these sublimation enthalpies are low [15], trends in these data are realistic. For the complexes listed in Table 4, the Be(II) complexes are more volatile than the corresponding Al(III) complexes and the present work indicates the same trend for the parent complexes. Trends in these data may be further refined in terms of the symmetry and polarity of the β-diketonate ligands [16].

Eisentraut and Sievers [17] have investigated the degree of volatility of a series of Al(III) β-diketonate complexes by thermogravimetry and report the following order of decreasing volatility: Al(hfac)$_3$ > Al(hfac)$_2$(acac) > Al(hfac)(acac)$_2$ > Al(tfac)$_3$ > Al(fod)$_3$ = Al(acac)$_3$ > Al(thd)$_3$. acac = 2,4-Pentanedione; hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; and fod =

TABLE 6

Sublimation enthalpies of Be(II) and Al(III) β-diketonate complexes (kJ mole^{-1})

Metal	Ligand [a]				
	tfac	bzac	btfac	Ftfac	Ttfac
Be(II)	30.46	19.71	16.44	32.55	
Al(III)	40.00	20.50	55.23		46.44

[a] tfac = 1,1,1-Trifluoro-2,4-pentanedione; bzac = 1-phenyl-1,3-butanedione; btfac = 1-phenyl-4,4,4-trifluoro-1,3-butanedione; Ftfac = 1-(2-Furoyl)-4,4,4-trifluoro-1,3-butanedione; Ttfac = 1-(2-Thenoyl)-4,4,4-trifluoro-1,3-butanedione.

1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione. Thus increasing the extent of ligand fluorine substitution increases the volatility of the corresponding metal complex.

Cavell and Pilcher [10] have determined the standard enthalpy of formation (298 K) of tris(2,4-pentanedionato)gallium(III) and tris(2,4-pentanedionato)indium(III) by combustion calorimetry and report $\Delta H_f^0[\text{Ga}(\text{C}_5\text{H}_7\text{O}_2)_3] = -1476.0$ kJ mole^{-1} and $\Delta H_f^0[\text{In}(\text{C}_5\text{H}_7\text{O}_2)_3] = 1405.7$ kJ mole^{-1}. The standard enthalpy of formation (298 K) of tris(2,4-pentanedionato)gallium(III) has also been determined by Irving and Walter [18] using solution calorimetry: $\Delta H_f^0[\text{Ga}(\text{C}_5\text{H}_7\text{O}_2)_3] = -1482.8$ kJ mole^{-1}. These data yield $\bar{D}(\text{Ga–O}) = 156$ kJ and $\bar{D}(\text{In–O}) = 137$ kJ. Thus for the triad Al, Ga, In, the metal–oxygen bond energies associated with the corresponding β-diketonate complexes decrease as the radius of the coordinated metal cation increases: Al(III), 67.5 pm; Ga(III), 76.0 pm and In(III), 94.0 pm [14]. This is an expected trend within a group of 'p-block' elements.

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