Thermochimica Acta, 72 (1984) 341–347
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DSC DETERMINATION OF THE FUSION AND SUBLIMATION ENTHALPY OF TRIS(2,4-PENTANEDIONATO)CHROMIUM(III) AND IRON(III)

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(Received 26 July 1983)

ABSTRACT

The sublimation enthalpy of tris(2,4-pentanedionato)chromium(III) and of tris(2,4-pentanedionato)iron(III) has been determined as 141.5 ± 5.6 kJ mol^{-1} and 103.9 ± 5.5 kJ mol^{-1}, respectively. The corresponding fusion enthalpies are 28.10 ± 1.28 kJ mol^{-1} and 22.65 ± 0.49 kJ mol^{-1}, respectively.

INTRODUCTION

Sublimation enthalpies of the title complexes quoted in the literature vary over a wide range. For tris (2,4-pentanedionato)chromium(III), Frankhauser [1] quotes $\Delta H_{sub} = 91.6 \pm 1.3$ kJ mol^{-1} based on effusion measurements; Jones and Wood [2] quote 27.6 ± 2.9 kJ mol^{-1} based on isoteniscopic measurements; Melia and Merrifield [3] quote 110.9 ± 0.8 kJ mol^{-1} based on the sublimation bulb/spectrophotometric technique; and Ashcroft [4] quotes 85.9 kJ mol^{-1} based on the thermogravimetric method. For tris(2,4-pentanedionato)iron(III), Berg and Truemper [5,6] quote $\Delta H_{sub} = 19.5$ kJ mol^{-1} based on isoteniscopic measurements; Farrar and Jones [7] quote 23.4 kJ mol^{-1} also based on isoteniscopic measurements; Melia and Merrifield [8] quote 99.0 ± 0.8 kJ mol^{-1} based on the sublimation bulb/spectrophotometric technique (Beech and Lintonbon [9] have derived the corresponding fusion enthalpy (34.1 ± 0.9 kJ mol^{-1}) and the vaporisation enthalpy (82 ± 1 kJ mol^{-1}) using DSC and a nitrogen atmosphere which yields the sublimation enthalpy as 116 ± 1 kJ mol^{-1}); Ashcroft [4] has quoted 114.9 kJ mol^{-1}

0040-6031/84/$03.00

based on thermogravimetric data; and Hill and Sachinidis [10] have quoted 112 ± 6 kJ mol^{-1} based on the isoteniscopic technique and 121 ± 5 kJ mol^{-1} based on the sublimation bulb/spectrophotometric technique. Hill and Sachinidis [10] reviewed the available sublimation enthalpy data for tris(2,4-pentanedionato)iron(III) and selected $\Delta H_{sub} = 113.6 \pm 3.8$ kJ mol^{-1} for the temperature range 335–356 K.

The fusion enthalpies of the title complexes have also been previously determined by DSC. Melia and Merrifield [3] quote $\Delta H_{fus} = 28.4 \pm 0.5$ kJ mol^{-1} for $(C_5H_7O_2)_3Cr$ and 25.9 ± 0.5 kJ mol^{-1} for $(C_5H_7O_2)_3Fe$. Beech and Lintonbon [9] quote $\Delta H_{fus} = 34.1 \pm 0.9$ kJ mol^{-1} for $(C_5H_7O_2)_3Fe$.

Murray et al. [11] have defined benzoic acid as a calibrant compound for the determination of sublimation enthalpies by DSC and this has allowed standardisation of the procedure, which has been subsequently employed [12] to determine the fusion and sublimation enthalpies of bis(2,4-pentanedionato)beryllium(II) and tris(2,4-pentanedionato)aluminium(III). Following a systematic redetermination of solid-state thermodynamic data for metal β-diketonate complexes, the fusion and sublimation enthalpies of tris(2,4-pentanedionato)chromium(III) and iron(III) are now reported, together with a review of published related data.

EXPERIMENTAL

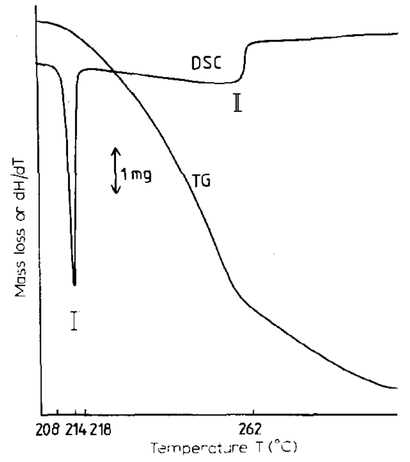
Tris(2,4-pentanedionato)chromium(III) was prepared according to the method of Fernelius and Blanch [13] and was recrystallised from benzene/petroleum ether 80:20 v/v. The product was sublimed prior to DSC study (m.p. 214: lit. 216°C [13]). Tris(2,4-pentanedionato)iron(III) was prepared according to the method of Berg and Truemper [5,6]. The product was purified by repeated sublimation. (m.p. 188: lit. 181°C [14]). Microanalysis data (Amdel Microanalytical Service, Melbourne, Australia) for these complexes are given in Table 1.

The DSC, calibration, sample preparation, experimental procedures and data analysis have been described in detail previously [12].

TABLE 1

Microanalysis data for Cr(III) and Fe(III) acetylacetonate complexes

Complex	Calculated (%)		Found (%)	
	C	H	C	H
$(C_5H_7O_2)_3Cr$	51.57	6.06	51.79	6.36
$(C_5H_7O_2)_3Fe$	51.01	5.99	50.76	6.24



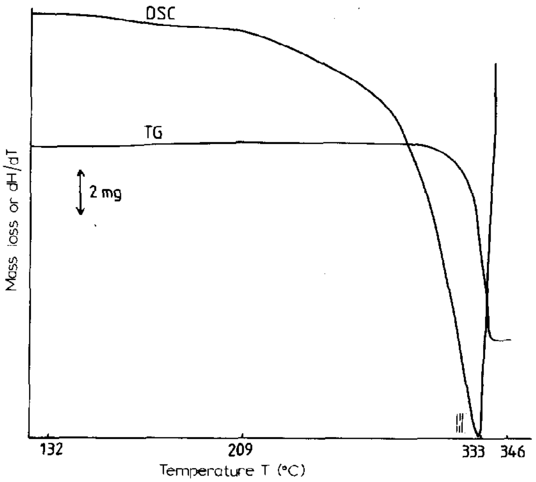


Fig. 1. Typical TG–DSC thermogram (nitrogen) of $(C_5H_7O_2)_3Cr$. Sample mass, 8.31 mg; fusion temperature, 214°C; vaporisation temperature range, 218–262°C.

Fig. 2. Typical TG–DSC thermogram (vacuum) of $(C_5H_7O_2)_3Cr$. Sample mass, 9.01 mg; sublimation temperature range, 209–346°C; sublimation peak temperature, 333°C.

RESULTS AND DISCUSSION

Representative TG–DSC thermograms for tris(2,4-pentanedionato)chromium(III) are shown in Figs. 1 and 2 and for tris(2,4-pentanedionato)iron(III) in Figs. 3 and 4. These thermograms are simple to interpret. In the case of thermal analysis using a nitrogen atmosphere (Figs. 1 and 3) fusion and vaporisation of the complexes are apparent (Peaks I and II, respectively) and

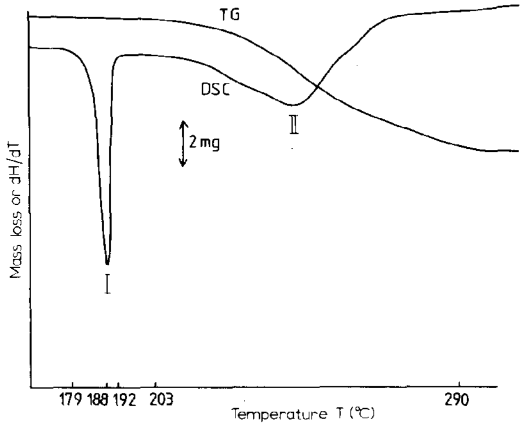


Fig. 3. Typical TG–DSC thermogram (nitrogen) of $(C_5H_7O_2)_3Fe$. Sample mass, 8.40 mg; fusion temperature, 188°C; vaporisation temperature range, 203–290°C.

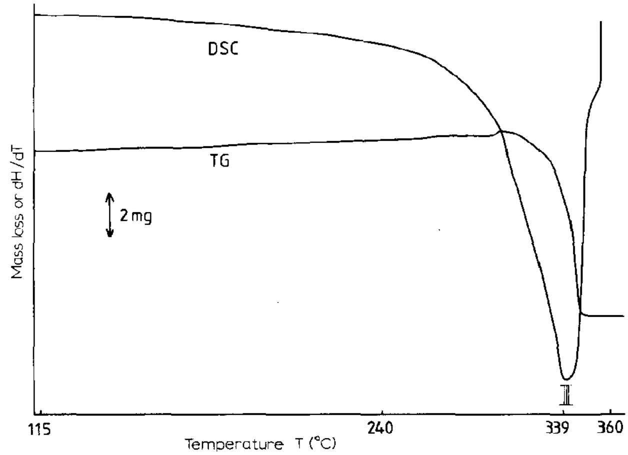


Fig. 4. Typical TG–DSC thermogram (vacuum) of $(C_5H_7O_2)_3Fe$. Sample mass, 8.62 mg; sublimation temperature range, 240–360°C; sublimation peak temperature, 339°C.

in the case of thermal analysis under vacuum (Figs. 2 and 4) smooth sublimation of the complexes only is apparent (Peak III), with the associated mass loss being equal to the initial sample mass. Fusion enthalpy data for the two complexes, as derived from Peak I areas in thermograms of the type shown in Figs. 1 and 3 are recorded in Tables 2 and 3 and corresponding sublimation enthalpy data as derived from Peak III areas in thermograms of the type shown in Figs. 2 and 4 are recorded in Tables 4 and 5.

In the case of fusion enthalpies, combination of the present data with all corresponding previous data yields a selected mean $\Delta H_{fus} = 28.3 \pm 0.2$ and 27.6 ± 5.9 kJ mol^{-1} for $(C_5H_7O_2)_3Cr$ and $(C_5H_7O_2)_3Fe$, respectively.

Similarly, for sublimation enthalpies, combination of the present data with selected previous data yields a mean $\Delta H_{sub} = 126.2 \pm 21.6$ and 111.3 ± 8.0 kJ mol^{-1} for $(C_5H_7O_2)_3Cr$ and $(C_5H_7O_2)_3Fe$, respectively. The new

TABLE 2

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

Sample mass (mg)	DSC range (m cal s^{-1})	ΔH_{fus} (kJ mol^{-1})
10.49	±8	29.11
7.62	±4	26.89
8.31	±8	29.13
8.02	±8	29.59
4.41	±4	27.65
11.25	±8	28.52
4.16	±2	25.79

Mean $\Delta H_{fus} = 28.10 \pm 1.28$ kJ mol^{-1}.

TABLE 3

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

Sample mass (mg)	DSC range (m cal s^{-1})	ΔH_{fus} (kJ mol^{-1})
7.16	±4	22.19
8.40	±4	23.46
6.39	±4	22.19
5.05	±4	23.07
7.31	±4	22.86
4.18	±2	22.03
4.56	±2	22.78

Mean $\Delta H_{fus} = 22.65 \pm 0.49$ kJ mol^{-1}.

TABLE 4

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

Sample mass (mg)	DSC range (m cal s^{-1})	ΔH_{sub} (kJ mol^{-1})
9.58	±4	138.8
10.76	±8	140.2
9.01	±4	142.4
8.96	±4	133.3
9.51	±4	132.6
5.43	±4	143.7
7.43	±4	149.8
6.89	±4	145.9
5.88	±4	138.9
10.13	±4	149.5

Mean $\Delta H_{sub} = 141.5 \pm 5.6$ kJ mol^{-1}.

TABLE 5

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

Sample mass (mg)	DSC range (m cal s^{-1})	ΔH_{sub} (kJ mol^{-1})
8.46	±8	98.85
5.93	±4	100.24
5.40	±4	100.98
5.02	±4	98.06
8.62	±4	102.70
10.59	±4	113.1
6.64	±4	104.91
7.08	±4	98.54
10.42	±4	108.8
11.03	±8	113.03

Mean $\Delta H_{sub} = 103.9 \pm 5.5$ kJ mol^{-1}.

mean ΔH_{sub} for $(C_5H_7O_2)_3Fe$ is within the limits of the selected value of Sachinidis and Hill [10].

It is appropriate to recalculate the Cr–O thermochemical bond energy based upon the currently selected sublimation enthalpy for tris(2,4-pentanedionato)chromium(III). Hill and Irving [15] reported $\Delta H_f^0(C_5H_7O_2)_3Cr = -1554.2 \pm 5.7$ kJ mol^{-1} based on solution calorimetric data which, in combination with $\Delta H_{sub}(C_5H_7O_2)_3Cr = 126.2$ kJ mol^{-1}, yields $\Delta H_{f(g)}^0(C_5H_7O_2)_3Cr = -1428.0$ kJ mol^{-1}. $\Delta H_{f(g)}^0 Cr = 296.0$ [16] and Cavell and Pilcher [17] calculated $\Delta H_f^0[C_5H_7O_{2(g)}] = -235.7$ kJ mol^{-1}. Thus, since all six chromium–oxygen bonds in tris(2,4-pentanedionato)chromium(III) are equal in length, $\bar{D}(Cr{-}O) = 186 \pm 6$ kJ. $\bar{D}(Fe{-}O)$ for tris(2,4-pentanedionato)iron(III), based on the selected $\Delta H_{sub} = 113.6 \pm 3.8$ kJ mol^{-1}, has been calculated previously [10].

It is relevant to note that Eisentraut and Sievers [18] reported a detailed thermogravimetric study of a series of chromium(III) and iron(III) β-diketonate complexes with the aim of establishing volatility trends with respect to variation of substituents on carbon atoms 1 and 3 of the β-diketone. For fluoro substituents on C_1, the volatility of the corresponding complexes is markedly increased compared to that of the parent acetylacetonate complexes, whereas a phenyl substituent at C_1 or an alkyl or bromo substituent at C_3 decreases volatility of Cr(III) and Fe(III) β-diketonate complexes.

Burkinshaw and Mortimer [19] recently reviewed the thermochemistry of transition metal β-diketonate complexes and have shown that for complexes of the type $(C_5H_7O_2)_2M$ and $(C_5H_7O_2)_3M$, where M is a first-row transition metal, the respective thermochemical metal–oxygen coordinate bond energies are consistent with the basic principles of the Crystal Field Theory.

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