Thermochimica Acta, 109 (1987) 391–396
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DSC DETERMINATION OF THE SUBLIMATION ENTHALPY OF BIS(2,4-PENTANEDIONATO)OXOVANADIUM(IV) AND TETRAKIS(2,4-PENTANEDIONATO)ZIRCONIUM(IV)

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(Received 27 May 1986)

ABSTRACT

The sublimation enthalpies of bis(2,4-pentanedionato)oxovanadium(IV) and tetrakis(2,4-pentanedionato)zirconium(IV) have been determined by differential scanning calorimetry as 140.7 ± 4.0 and 132.0 ± 6.8 kJ mol^{-1}, respectively. The fusion enthalpy of the latter complex has also been determined as 33.68 ± 2.5 kJ mol^{-1}. A summary of "selected" sublimation enthalpy data for first-row transition metal acetylacetonate complexes is included.

INTRODUCTION

No empirical sublimation enthalpy data exist for the title complexes. Jones et al. [1] have estimated $\Delta H_{sub}(C_5H_7O_2)_2VO$ as 62.8 kJ mol^{-1} by comparison with that for the structurally related complexes $(C_5H_7O_2)_2Co$ and $(C_5H_7O_2)_2Ni$ as derived by Berg and Truemper [2] using the isoteniscopic method. Beech and Lintonbon [3] have determined, by DSC, the fusion enthalpy of bis(2,4-pentanedionato)oxovanadium(IV) as 34 ± 1 kJ mol^{-1} and have additionally reported that sublimation of this complex is associated with decomposition.

The present determination of the sublimation enthalpy of bis(2,4-pentanedionato)oxovanadium(IV) and tetrakis(2,4-pentanedionato)zirconium(IV) represents the conclusion of a systematic redetermination of the sublimation enthalpies of metal acetylacetonate complexes by DSC [4,5]. A brief review of the subject is also presented.

0040-6031/87/$03.50

TABLE 1

Microanalysis data for VO(II) and Zr(IV)acetylacetonate complexes

Complex	Calculated %		Found %	
	C	H	C	H
$(C_5H_7O_2)_2VO$	45.3	5.3	45.6	5.6
$(C_5H_7O_2)_4Zr$	49.3	5.8	49.6	5.9

EXPERIMENTAL

Bis(2,4-pentanedionato)oxovanadium(IV) was prepared according to the method of Fernelius and Bryant [6] and was twice recrystallised from chloroform. Tetrakis(2,4-pentanedionato)zirconium(IV) was obtained from Merck (Synthesis Grade) and was twice recrystallised from benzene/petroleum ether, 80 : 20 v/v (m.p. 193–196°C). 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 [7].

RESULTS AND DISCUSSION

A typical DSC thermogram for bis(2,4-pentanedionato)oxovanadium(IV) is shown in Fig. 1 and the derived enthalpy data are recorded in Table 2.

This represents the first empirical determination of $\Delta H_{sub}(C_5H_7O_2)_2VO$.

A typical TG/DSC thermogram for tetrakis(2,4-pentanedionato)zirconium(IV) is shown in Fig. 2 and the derived sublimation enthalpy data are recorded in Table 3.

The mass loss over the sublimation range 140–190°C corresponds to 100% and thus sublimation without decomposition is confirmed for $(C_5H_7O_2)_4Zr$. This represents the first empirical determination of ΔH_{sub}-$(C_5H_7O_2)_4Zr$.

The fusion enthalpy of tetrakis(2,4-pentanedionato)zirconium(IV) has also been determined by DSC, using a dynamic nitrogen atmosphere for thermal analysis and indium ($\Delta H_{Fus} = 3.29 \pm 0.01$ kJ mol^{-1}) as calibrant. The derived data are recorded in Table 4.

$\Delta H_{Fus}(C_5H_7O_2)_4Zr = 33.68 \pm 2.5$ kJ mol^{-1} is in excellent agreement with the value, 34 ± 1 kJ mol^{-1}, previously determined by Beech and Lintonbon [3].

The vaporisation peak for this complex is broad and corresponds to the range 194–275°C. No meaningful vaporisation enthalpy can be derived therefrom.

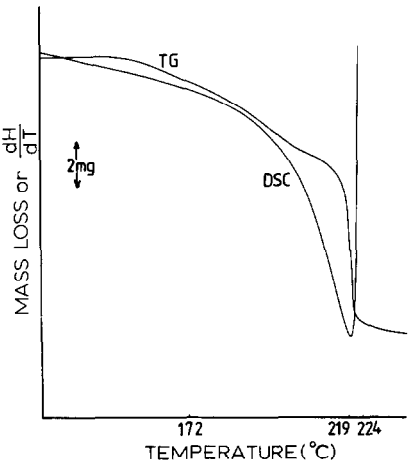

Fig. 1. Typical DSC thermogram of $(C_5H_7O_2)_2VO$. Sample mass, 7.39 mg; sublimation temperature range, 140–230°C; sublimation peak temperature, 220°C.

It is relevant to review briefly the sublimation/vaporisation studies previously reported for vanadium(III) and oxovanadium(IV) β-diketonate complexes.

Melia and Merrifield [8] have determined the sublimation enthalpy of tris(2,4-pentanedionato)vanadium(III) using the sublimation bulb technique: $\Delta H_{sub} = 102.9 \pm 0.8$ kJ mol^{-1} (298 K). Beech and Lintonbon [3], using mass spectrometry, have concluded that this complex decomposes in vacuum and have derived by DSC a vaporisation enthalpy of 197 ± 6 kJ mol^{-1}.

Dilli and Patsalides [9] have studied the volatility characteristics of a wide range of substituted vanadium(III) and oxovanadium(IV) β-diketonate com-

TABLE 2

Sublimation enthalpy data for bis(2,4-pentanedionato)oxovanadium(IV)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{sub} (kJ mol^{-1})
7.39	±4	134.9
17.93	±8	138.4
15.35	±8	147.4
13.36	±8	139.9
13.24	±8	144.1
12.64	±8	138.2
16.98	±8	145.0
16.27	±8	135.3
11.83	±4	139.6
20.44	±16	144.0
		Mean = 140.7 ± 4.0

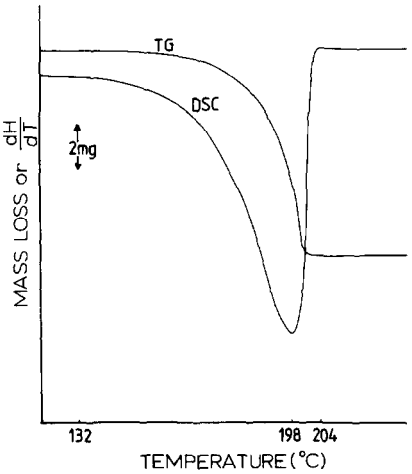

Fig. 2. Typical TG–DSC thermogram of $(C_5H_7O_2)_4Zr$. Sample mass, 9.38 mg; sublimation temperature range, 140–190°C; sublimation peak temperature, 180°C.

TABLE 3

Sublimation enthalpy data for tetrakis(2,4-pentanedionato)zirconium(IV)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{sub} (kJ mol^{-1})
14.16	±4	121.5
6.22	±4	130.7
10.22	±8	133.5
8.54	±4	133.7
8.55	±4	128.2
9.47	±4	142.7
6.82	±4	132.7
6.56	±4	141.0
9.38	±4	120.8
8.32	±4	135.4
		Mean = 132.0 ± 6.8

TABLE 4

Fusion enthalpy data for tetrakis(2,4-pentanedionato)zirconium(IV) (m.p. 190°C)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{Fus} (kJ mol^{-1})
7.20	±2	36.15
13.04	±2	37.17
9.90	±2	31.51
6.25	±2	31.33
8.28	±4	32.24
		Mean = 33.68 ± 2.5

TABLE 5

Summary of sublimation enthalpies of first-row transition metal acetylacetonate complexes

$(C_5H_7O_2)_nM$	ΔH_{sub}(kJ mol^{-1})									
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$n=2$		D [b]	140.7 [d]		D [b]			111.9 [f]	98.1 [f]	117.0 [g]
$n=3$	98.4 [a]		102.9 [c]	141.5 [e]	D [b]	103.9 [c]	142.6 [f]			

[a] Mean value from refs. 8 and 12.
[b] Decomposition, ref. 3.
[c] From ref. 8.
[d] For $VO(acac)_2$, present paper.
[e] From ref. 5.
[f] From ref. 13.
[g] From ref. 14.

plexes by TG/DTA. The fluorinated vanadium(III) complexes appeared to sublime without decomposition whereas decomposition was associated with the oxovanadium(IV) complexes. The volatility data are interpreted in terms of the inductive and steric effects of the ligand substituents.

Sublimation enthalpy data for second and third-row transition metal acetylacetonate complexes are sparse. In addition to $\Delta H_{sub}(C_5H_7O_2)_4Zr$ reported here, Burkinshaw and Mortimer [10] have reported sublimation enthalpies for $(C_5H_7O_2)_2M$, with M=Pd(II), Pt(II) and Cd(II), as 127.6 ± 17, 129.4 ± 9 and 144.9 ± 22 kJ mol^{-1}, respectively, using the Knudsen effusion method.

Despite some controversy with respect to the sublimation characteristics of Ti(IV), V(III), Mn(II) and Mn(III) acetylacetonate complexes, sublimation enthalpies for the remaining first-row transition metal acetylacetonate complexes appear to be well established and "selected" values for these complexes are given in Table 5. These data, in conjunction with other empirical calorimetric data, permit derivation of metal–oxygen thermochemical bond energies and crystal field stabilisation energies for these complexes. A recent exposition of this approach for first-row divalent transition metal acetylacetonates has been provided by Kakolowicz and Giera [11].

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