Thermochimica Acta, 35 (1980) 59—66

A RE-EVALUATION OF THE ENTHALPY OF SUBLIMATION OF SOME METAL ACETYLACETONATE COMPLEXES

J. SACHINIDIS and J.O. HILL

Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Victoria 3083 (Australia)

(Received 27 March 1979)

ABSTRACT

Sublimation enthalpies for Al(III), Fe(III) and Zn(II) acetylacetonates derived using isoteniscopic, sublimation bulb and spoon gauge techniques are reported. Selected sublimation enthalpies are $Al(C_5H_7O_2)_3$, 118.6 ± 7.8; $Fe(C_5H_7O_2)_3$, 113.6 ± 3.8; and $Zn(C_5H_7O_2)_2$, 117 ± 3 kJ $mole^{-1}$, respectively.

INTRODUCTION

Large discrepancies exist between reported enthalpies of sublimation for metal acetylacetonate complexes and, further, enthalpies of sublimation derived for the same complex by different techniques are generally inconsistent. For example, the published ΔH_{sub} values for tris(acetylacetonato)iron(III) range from 19.5 kJ $mole^{-1}$ [1] obtained by the isoteniscopic method to 116.0 kJ $mole^{-1}$ [2] obtained by differential scanning calorimetry, with several values scattered between these extremes [3—5].

This paper reports new sublimation enthalpy data for the acetylacetonate complexes of Al(III), Fe(III) and Zn(II) as derived using upgraded isoteniscopic, spoon gauge and sublimation bulb techniques.

EXPERIMENTAL

Isoteniscope

An upgraded version of the Smith—Menzies isoteniscope [6] was used. The reference and sample segments of the conventional isoteniscope were interconnected to the main vacuum line capable of producing a vacuum of $5 \cdot 10^{-3}$ torr as measured by an Edwards, Model M5C-2 Pirani gauge head coupled to an Edwards, Model 8-2 Pirani gauge. This simple modification to the isoteniscope allowed efficient degassing of sample and manometric fluid and ensured equilibration of pressure in the reference and sample arms prior to commencement of sublimation of the sample. A greaseless teflon needle valve was positioned at the top of the sample chamber to allow easy addition and removal of sample. Triply-distilled mercury was employed as the manometric fluid. Sample masses of approximately 20 mg were used. The thermostat contained Shell "Ondina 33" oil (flash-point 195°C). Temperature control (±0.05°C) was effected using a Utah Electronics H2-7 temperature controller in conjunction with a 2000-ohm rapid response thermistor. The thermostat heater consisted of a nichrome wire coil contained in a glass helix filled with "ondina" oil. Temperatures were measured using calibrated Zum Ultra, mercury-in-glass, 170 mm, fixed immersion thermometers. Typically, a 4-h degassing period was employed at temperatures up to 100°C. Solid—vapour equilibrium was normally attained within a 30-min period and the difference between the mercury levels in the reference arm of the isoteniscope was determined using a Precision Tool Instrument Co. cathetometer (Type 2207). A minimum of five vapour pressure/temperature data points were recorded. Such data were corrected for the vapour pressure of mercury as obtained from "blank" experiments.

Spoon gauge

A double spoon gauge of design described by Swanwick [7] was employed. Pointer deflection was observed using a P.T.I. cathetometer (Type 2207) and vapour pressures were determined using an oil manometer of the type described by Veillon [8]; D.C. 704 diffusion pump oil served as manometric fluid; the density, 1.06 [8], corresponds to a sensitivity of 12.7 mm oil torr^{-1}. Efficient degassing of the oil was achieved with a glass-coated magnetic stirrer "follower" sealed inside the oil manometer. The gauge was operated as a null instrument and vapour-pressure measurements on the degassed sample (20 mg) were made according to the general procedure of Wolf et al. [9]. Separate "blank" experiments revealed that the spoon gauge was free of hysteresis. The gauge sensitivity was 3 mm torr^{-1}. The pointer deflection/effective vapour-pressure relationship for the gauge is expressed by the linear, zero intercept equation, $P = 0.3174D$, where D is the deflection (mm) and P is the effective vapour pressure (torr). The systematic error associated with a vapour-pressure measurement is ±0.004 torr as derived from the error in pointer deflection, ±0.01 mm, and the corresponding error in oil manometer levels, ±0.04 mm. The gauge was tested by measuring the vapour pressure of benzoic acid at four temperatures and the vapour pressure of ferrocene at 335.8 K. The data are recorded in Table 1.

The benzoic acid data are represented by the equation

$$\log_{10}P = 11.99 - 4434\ T^{-1}$$

yielding ΔH_{sub} (benzoic acid) = 85 ± 2 kJ mole^{-1}.

Sublimation bulb

The Melia—Merrifield [12] sublimation bulb and the associated experimental technique have been described in detail previously. Sample masses of

TABLE 1

Vapour pressure/temperature data for benzoic acid and ferrocene using the spoon gauge technique

	Temp. (K)	Vapour pressure (torr)	Lit. (torr)
Benzoic acid	344.4	0.126	0.143[10]
	352.8	0.283	0.291[10]
	373.7	1.257	1.231[10]
	393.8	5.502	5.530[10]
Ferrocene	335.8	0.183	0.188[11]

approximately 20 mg were employed. In all cases the measured absorbances were converted to sublimation pressure by substitution of the measured values in the equation

$$P = \frac{62.365 A V_s T}{V_T \epsilon d} \tag{1}$$

where A is the absorbance of the extract at a selected wavelength, V_s is the volume of solvent introduced into the bulb, T is the temperature of measurement in K, V_T is the volume of the bulb at the temperature of measurement, ϵ is the molar extinction coefficient of the sample under investigation at the selected wavelength (determined in calibration experiments) and d is the path length in cm.

A least-squares treatment of the vapour pressure/temperature data was applied to compute values of the constants A and B in the linear equation

$$\log_{10}P = A - BT^{-1}$$

and hence ΔH_{sub} for the test compound. The bulb was tested by determining the sublimation enthalpy of benzoic acid. Ethanol solutions of condensed benzoic acid were analysed using a Varian-Techtron 635D, UV—visible absorption spectrophotometer. The selected analytical wavelength was the 272 nm absorption band ($\epsilon = 846.1$). The relevant vapour pressure/temperature data are shown in Table 2 and are described by the equation

$$\log_{10}P = 12.45 - 4605\ T^{-1}$$

yielding ΔH_{sub} (benzoic acid) = 88.1 ± 2.0 kJ mole^{-1}, which is in excellent agreement with the value 91.5 kJ mole^{-1} reported by Davies and Jones [13].

For the metal acetylacetonate complexes, methyl-isobutylketone (MIBK) or di-isobutylketone (DIBK) condensate solutions were analysed for metal concentration using a Varian-Techtron AA5 atomic absorption spectrophotometer employing an air—acetylene or a nitrogen—acetylene flame.

The metal acetylacetonate complexes were synthesised by well-established procedures and were purified by repeated sublimation. $Al(C_5H_7O_2)_3$: m.p. 94—195, literature 194.6°C [14]; $Fe(C_5H_7O_2)_3$: m.p. = 181.0—181.5, litera-ure 181°C [15]; $Zn(C_5H_7O_2)_3$: m.p. 126.5, literature 127°C (anhydrous) [16]. A TG/DTA analysis of the sublimed zinc acetylacetonate sample

TABLE 2

Vapour pressure/temperature data for benzoic acid using the sublimation bulb technique

Temp. (K)	Absorbance	Vapour pressure (torr)
333.8	0.119	0.054
338.7	0.158	0.073
344.7	0.259	0.121
350.1	0.418	0.199
353.8	0.568	0.273
360.8	1.004	0.492

revealed a water content of less than 1.0 weight %. Benzoic acid (B.D.H. analar grade), ferrocene (Merck, synthesis grade) and naphthalene (Merck, scintillation grade) were purified by repeated sublimation: benzoic acid: m.p. 122.4, literature 122.4°C [17]; naphthalene: m.p. 80.5, literature 80.55°C [17].

RESULTS

Aluminium acetylacetonate

The relevant vapour pressure/temperature data as obtained by the spoon gauge technique are recorded in Table 3 and are described by the equation

$$\log_{10}P = 13.521 - 5794T^{-1}$$

yielding $\Delta H_{sub}[Al(C_5H_7O_2)_3] = 111 \pm 4$ kJ mole^{-1} (388—413 K).

The relevant vapour pressure/temperature data for $Al(C_5H_7O_2)_3$ as obtained by the sublimation bulb technique are given in Table 4. The condensate was dissolved in 10 cm^3 MIBK. The selected analytical wavelength was the 309.2 nm absorption band ($\epsilon = 514.6$). The data are described by the

TABLE 3

Vapour pressure/temperature data fer $Al(C_5H_7O_2)_3$ using the spoon gauge technique

Temp. (K)	Pointer deflection (mm)	Oil manometer (mm oil)	Vapour pressure (torr)	Pirani Gauge (torr)
388.7	0.13	0.52	0.041	0.043
393.3	0.20	0.83	0.065	0.060
394.0	0.19	0.83	0.065	0.066
398.0	0.26	1.15	0.090	0.100
402.7	0.40	1.62	0.128	0.135
408.7	0.68	2.78	0.219	0.220
412.9	1.00	4.06	0.320	0.350

TABLE 4

Vapour pressure/temperature data for $Al(C_5H_7O_2)_3$ using the sublimation bulb technique

Temp. (K)	Absorbance	Vapour pressure (torr)
388.7	0.085	0.0365
395.9	0.150	0.0650
403.5	0.270	0.1200

equation

$$\log_{10}P = 12.653 - 5478T^{-1}$$

yielding $\Delta H_{sub}[Al(C_5H_7O_2)_3] = 105 \pm 2$ kJ mole^{-1} (388—404 K).

Ferric acetylacetonate

The relevant vapour pressure/temperature data as obtained by the isoteniscopic technique are recorded in Table 5 and are described by the equation

$$\log_{10}P = 14.790 - 5845T^{-1}$$

yielding $\Delta H_{sub}[Fe(C_5H_7O_2)_3] = 112 \pm 6$ kJ mole^{-1} (381—402 K).

The relevant vapour pressure/temperature data as obtained by the sublimation bulb technique are recorded in Table 6. The condensate was dissolved in 10 cm^3 MIBK. The selected analytical wavelength was the 248.3 nm absorption band ($\epsilon = 3836.2$). The data are described by the equation

$$\log_{10}P = 14.222 - 6331T^{-1}$$

yielding $\Delta H_{sub}[Fe(C_5H_7O_2)_3] = 121 \pm 5$ kJ mole^{-1} (373—402 K).

Zinc acetylacetonate

The relevant vapour pressure/temperature data as obtained by the sublimation bulb technique are recorded in Table 7. The condensate was dis-

TABLE 5

Vapour pressure/temperature data for $Fe(C_5H_7O_2)_3$ using the isoteniscopic technique

Temp. (K)	Vapour pressure (torr)
381.0	0.25
386.0	0.53
390.0	0.65
395.5	0.95
396.0	1.11
401.5	1.69

TABLE 6

Vapour pressure/temperature data for $Fe(C_5H_7O_2)_3$ using the sublimation bulb technique

Temp. (K)	Absorbance	Vapour pressure (torr)
373.6	0.0333	0.0020
381.2	0.075	0.004
388.5	0.145	0.008
394.2	0.245	0.015
401.7	0.515	0.031

solved in DIBK. The selected analytical wavelength was the 213.8 nm absorption band (ϵ = 22568.8). The data are described by the equation

$$\log_{10}P = 15.770 - 6131T^{-1}$$

yielding $\Delta H_{sub}[Zn(C_5H_7O_2)_2]$ = 117 ± 3 kJ mole^{-1} (337—362 K).

It is of significance to review the published ΔH_{sub} data for Al(III), Fe(III) and Zn(II)acetylacetonates and hence to propose a "selected value" for each complex. For aluminium acetylacetonate, the isoteniscopic ΔH_{sub} = 20.5 kJ mole^{-1} (temperature range 417—476 K) as obtained by Berg and Truemper [1] is widely divergent from more recent data. Beech and Lintonbon [2] have measured the fusion enthalpy (35 ± 2 kJ mole^{-1}) and vaporisation enthalpy (94 ± 6 kJ mole^{-1}) of aluminium acetylacetonate in a nitrogen atmosphere using DSC, which yielded $\Delta H_{sub}[Al(C_5H_7O_2)_3]$ = 129 ± 8 kJ mole^{-1} (temperature range 460—548 K). Irving and Ribeiro da Silva [18] have reported $\Delta H_{sub}[Al(C_5H_7O_2)_3]$ = 121.7 ± 4.2 kJ mole^{-1} at 298 K. Neglecting the data of Berg and Truemper and allowing for the nitrogen atmosphere associated with the data of Beech and Lintonbon, we select $\Delta H_{sub}[Al(C_5H_7O_2)]$ = 118.6 ± 7.8 kJ mole^{-1} as representing the mean and standard deviation of all recent experimental data, and applicable to the effective temperature range of 390—550 K.

For ferric acetylacetonate, similarly, the isoteniscopic ΔH_{sub} = 19.5 kJ mole^{-1} as obtained by Berg and Truemper [1] (temperature range not given) and ΔH_{sub} = 23.4 kJ mole^{-1} (temperature range not given) as obtained by Farrar and Jones [5], although in close agreement, are considerably divergent from more recent data. Melia and Merrifield [3] have reported ΔH_{sub}-

TABLE 7

Vapour pressure/temperature data for $Zn(C_5H_7O_2)_2$ using the sublimation bulb technique

Temp. (K)	Absorbance	Vapour pressure (torr)
337.4	0.250	0.004
344.8	0.565	0.010
353.2	0.555	0.025
361.3	0.705	0.065

$[Fe(C_5H_7O_2)_3]$ = 99.0 ± 0.8 kJ mole^{-1} (temperature range 378—405 K), as obtained by the sublimation bulb technique, and Beech and Lintonbon [2] have derived the fusion enthalpy (34.1 ± 0.9 kJ mole^{-1}) and the vaporisation enthalpy (82 ± 1 kJ mole^{-1}) in a nitrogen atmosphere using DSC which yielded $\Delta H_{sub}[Fe(C_5H_7O_2)_3]$ = 116 ± 1 kJ mole^{-1} (temperature range 452—535 K). This is in good agreement with the thermogravimetric value of $\Delta H_{sub}[Fe(C_5H_7O_2)_3]$ = 114.9 kJ mole^{-1} [19] (temperature range 335—356 K). Neglecting the isoteniscopic data, we select $\Delta H_{sub}[Fe(C_5H_7O_2)_3]$ = 113.6 ± 3.8 kJ mole^{-1} representing the mean and standard deviation of the recent experimental data and applicable to the temperature range of 335—356 K. For zinc acetylacetonate, only the fusion enthalpy 25.9 ± 2 kJ mole^{-1} and the vaporisation enthalpy 48 ± 2 kJ mole^{-1} as obtained by DSC have been published and these data refer to the monohydrate ΔH_{sub} $[Zn(C_5H_7O_2)_2 \cdot H_2O]$ = 74 ± 2 kJ mole^{-1} (temperature range 380—520 K). Our value for $\Delta H_{sub}[Zn(C_5H_7O_2)_2]$ = 117 ± 3 kJ mole^{-1} (temperature range 337—361 K) is the only datum available for the essentially anhydrous complex.

No heat capacity data are available to correct these sublimation enthalpies to 298 K. Enthalpies of sublimation of metal acetylacetonates are required for the derivation of thermochemical metal—oxygen coordinate bond energies in these complexes and it appears that the error resulting from neglecting the variation of ΔH_{sub} with temperature forms an insignificant contribution to the uncertainty interval associated with the metal—oxygen bond energy. This is revealed by the recalculated D(M—O) values for aluminium acetylacetonate and ferric acetylacetonate as derived from the original data of Hill and Irving [20,21] using updated data for the standard enthalpy of formation and sublimation of the complexes and the enthalpy of vaporisation of acetylacetone [22] (Table 8).

The new value for $\Delta H_f^0[Al(C_5H_7O_2)_3]$ is based on the corresponding enthalpy of combustion: ΔH_c^0 = 7948.4 ± 1.1 kJ mole^{-1} as reported by Cavell and Pilcher [23]. The combined data yield D(Al—O), the homolytic metal—oxygen bond energy, as 283.2 kJ mole^{-1}, as compared to D(Al—O) = 276.1 kJ mole^{-1} reported by Hill and Irving [20] based essentially on ΔH_{sub} $[Al(C_5H_7O_2)_3]$ = 19.2 kJ mole^{-1}. Similarly, using our selected ΔH_{sub} $[Fe(C_5H_7O_2)_3]$, D(Fe—O) = 195.1 kJ mole^{-1} compared to D(Fe—O) = 188.2 kJ mole^{-1} as reported by Hill and Irving [21] based essentially on ΔH_{sub} $[Fe(C_5H_7O_2)_3]$ = 65.3 kJ mole^{-1}. These differences in D(M—O) values result-

TABLE 8

Enthalpy data for Al(III) and Fe(III) acetylacetonate complexes and acetylacetone

Compound	ΔH_f^0 (kJ mole^{-1})	ΔH_{sub} (kJ mole^{-1})	ΔH_{vap} (kJ mole^{-1})
$Al(C_5H_7O_2)_3$	1793.3 ± 2.0	118.6 ± 7.8	—
$Fe(C_5H_7O_2)_3$	1310.4 ± 3.0	113.6 ± 3.8	—
$C_5H_8O_2$	—	—	43.2 ± 0.1

ing from the incorporation of more recent ΔH_{sub} data into the relevant first-law enthalpy calculations are within the overall experimental error and thus for practical purposes, variation of ΔH_{sub} with temperature for metal acetylacetonate complexes may be neglected.

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