Thermochimica Acta, 44 (1981) 213—222
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

A THERMODYNAMIC STUDY OF THE SUBLIMATION PROCESSES OF ALUMINIUM AND COPPER ACETYLACETONATES

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(Received 4 September 1980)

ABSTRACT

The vapor pressures of aluminium and copper acetylacetonates were measured in the temperature ranges 337—405 K and 316—445 K, respectively, by using the torsion effusion method. The corresponding sublimation enthalpies, $\Delta H^0_{298} = 47 \pm 1$ kJ mole^{-1} for aluminium acetylacetonate and $\Delta H^0_{298} = 57 \pm 1$ kJ mole^{-1} for copper acetylacetonate, were derived by treating the vapor pressure data by the so-called second- and third-law methods of thermodynamics. Heat capacity measurements were carried out for the solid complexes from 4.2 to 450 K. The thermodynamic functions of the solid phase were derived from the measured heat capacity values and those of the vapor phase from spectroscopic and structural data.

INTRODUCTION

The vapor pressure measurements of some acetylacetonates were carried out by several authors in connection with the possibility of separating various mixtures of metal diketone chelates by fractional sublimation or gas chromatography. The vapor pressure data reported in the literature were mainly derived by isoteniscopic methods [1,2]. However, for a series of these chelates the sublimation heats are not available. This is the case for copper acetylacetonate [$Cu(acac)_2$], while for aluminium acetylacetonate [$Al(acac)_3$] rather different values for the sublimation enthalpy have been proposed [1—3]. To complete these thermochemical data, we have undertaken this study by employing torsion effusion and the calorimetric techniques in order to evaluate the vapor pressures and the standard sublimation enthalpies of these chelates.

EXPERIMENTAL AND RESULTS

The samples were prepared following the procedure reported in the literature [4] and purified by sublimation under vacuum for several hours.

0040-6031/81/0000—0000/$ 02.50

Vapor pressure measurements

The basis and the experimental procedure of the torsion effusion method have been reported previously [5]. When the sample is heated at a given temperature in a particular Knudsen cell, the corresponding vapor pressure is derived by measuring the torsion angle α of a tungsten wire to which it is suspended by employing the following relation

$$P(\text{kPa}) = \frac{2K\alpha}{(a_1 l_1 f_1 + a_2 l_2 f_2)L} = K^0\alpha$$

where K is the constant of the torsion wire ($K = 0.346$ dyne cm rad^{-1}), a_1 and a_2 are the areas of the effusion holes, l_1 and l_2 are the respective distances from the rotation axis, f_1 and f_2 are the corresponding geometrical factors, and L is the torsion wire length. The correction factors are evaluated from the equation [6]

$$1/f = 0.0147(R/r)^2 + 0.3490(R/r) + 0.9982$$

where R and r are the thickness and the radius of the effusion hole, respectively.

The temperature of the cell was measured by a calibrated chromel—alumel thermocouple inserted in a second cell placed below the torsion cell. The measurements were performed using two graphite cells with different geometrical constants: cell A, $K^0 = (3.98 \pm 0.25) \times 10^{-5}$ kPa deg^{-1}; cell B, $K^0 = (2.63 \pm 0.25) \times 10^{-4}$ kPa deg^{-1}. The vapor pressures of standard elements (sulfur and mercury) were measured with these cells and the obtained data were compared with those reported in the literature [7] in order to test if the thermodynamic conditions, the temperature measurements and the geometrical factors used are reliable.

Vapor pressure data in the temperature range 337—405 K for $Al(acac)_3$ and 316—445 K for $Cu(acac)_2$ were derived. Average vapor pressure values obtained at each temperature from various experimental measurements are reported in Tables 1 and 2 and plotted in Figs. 1 and 2 as $\log P$ vs. $1/T$. The experimental data were treated by using the least squares method and yielded the following equations

$Al(acac)_3$	$\log P(\text{kPa}) = 3.34 \pm 0.10 - (2326 \pm 22)/T$	Cell A
	$\log P(\text{kPa}) = 3.54 \pm 0.20 - (2346 \pm 78)/T$	Cell B
$Cu(acac)_2$	$\log P(\text{kPa}) = 4.80 \pm 0.05 - (2826 \pm 20)/T$	Cell A
	$\log P(\text{kPa}) = 4.80 \pm 0.05 - (2831 \pm 25)/T$	Cell B

Heat capacity measurements

The heat capacities of the compounds were determined in two separate experiments. The measurements from 298 to 450 K were made employing a Perkin-Elmer DSC-2 differential calorimeter and those from 298 to 4.2 K were carried out in a calorimeter for cryogenic measurements equipped with a Mark II cryostat [8].

TABLE 1

Vapor pressure and third-law ΔH°_{298} values of aluminium acetylacetonate

T (K)	No. of point	P (kPa)	$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ (J mole^{-1} K^{-1})	ΔH°_{298} (kJ mole^{-1})
Cell A				
337	1	2.79×10^{-4}	31.51	46.50
340	2	3.16×10^{-4}	31.47	46.55
343	1	3.64×10^{-4}	31.43^5	46.54
346	3	4.12×10^{-4}	31.39	46.57
348	2	4.93×10^{-4}	31.36	46.31
350	1	4.94×10^{-4}	31.33	46.56
351	2	5.01×10^{-4}	31.32	46.65
354	2	5.73×10^{-4}	31.28	46.64
355	1	5.89×10^{-4}	31.26	46.69
359	2	7.94×10^{-4}	31.21	46.30
364	3	8.22×10^{-4}	31.14	46.82
368	2	1.06×10^{-3}	31.08	46.53
370	2	1.09×10^{-3}	31.05	46.69
372	1	1.18×10^{-3}	31.02	46.69
380	3	1.74×10^{-3}	30.91	46.42
382	2	1.99×10^{-3}	30.88	46.22
385	2	2.04×10^{-3}	30.84	46.49
388	1	2.21×10^{-3}	30.80	46.58
391	2	2.38×10^{-3}	30.76	46.69
393	2	2.61×10^{-3}	30.73	46.62
395	1	2.82×10^{-3}	30.70	46.59
Cell B				
357	2	6.31×10^{-4}	31.23	46.71
361	1	7.96×10^{-4}	31.18	46.54
367	3	1.06×10^{-3}	31.09	46.42
369	2	1.08×10^{-3}	31.07	46.58
374	2	$1.26^5 \times 10^{-3}$	30.99	46.73
375	1	1.47×10^{-3}	30.98	46.36
378	2	1.50×10^{-3}	30.94	46.65
381	1	1.78×10^{-3}	30.90	46.47
387	3	2.17×10^{-3}	30.81	46.52
390	2	2.27×10^{-3}	30.77	46.72
392	2	2.47×10^{-3}	30.74	46.68
394	1	2.70×10^{-3}	30.71	46.62
396	1	3.26×10^{-3}	30.69	46.22
397	1	3.29×10^{-3}	30.67	46.30
399	2	3.30×10^{-3}	30.64	46.50
400	1	3.36×10^{-3}	30.63	46.56
403	2	3.91×10^{-3}	30.59	46.39
405	1	4.04×10^{-3}	30.56	46.50
			Average	46.55 ± 0.15

In both cases a known weight of alumina (99.98% pure) was used as standard reference material. The temperature of the sample and of the standard reference was measured in the first case with calibrated iron—constantan

TABLE 2

Vapor pressure and third-law ΔH^0_{298} values of copper acetylacetonate

T (K)	No. of points	P (kPa)	$-\Delta(G^0_T - H^0_{298})/T$ (J mole^{-1} K^{-1})	ΔH^0_{298} (kJ mole^{-1})
Cell A				
316	2	7.21×10^{-5}	61.25	56.55
318	1	7.85×10^{-5}	61.21	56.67
320	2	9.12×10^{-5}	61.16	56.61
321	1	9.95×10^{-5}	61.11	56.54
323	1	1.13×10^{-4}	61.06	56.54
325	2	1.29×10^{-4}	60.96	56.53
330	2	1.70×10^{-4}	60.87	56.33
334	3	2.19×10^{-4}	60.77	56.53
338	2	2.77×10^{-4}	60.68	56.52
340	1	3.09×10^{-4}	60.65	56.53
347	3	4.47×10^{-4}	60.48	56.51
353	3	5.49×10^{-4}	60.35	56.50
356	2	7.31×10^{-4}	60.29	56.50
366	3	1.24×10^{-3}	60.00	56.39
370	2	1.43×10^{-3}	59.91	56.53
379	3	2.25×10^{-3}	59.72	56.40
383	2	2.60×10^{-3}	59.68	56.53
390	3	3.56×10^{-3}	59.62	56.52
397	2	4.66×10^{-3}	59.54	56.63
400	2	5.30×10^{-3}	59.52	56.60
402	2	6.03×10^{-3}	59.52	56.46
411	1	8.20×10^{-3}	59.47	56.65
412	1	8.63×10^{-3}	59.46	56.61
Cell B				
342	2	3.44×10^{-4}	60.58	56.52
350	2	5.32×10^{-4}	60.39	56.50
359	3	8.43×10^{-4}	60.19	56.53
363	3	9.95×10^{-4}	60.10	56.62
374	3	1.73×10^{-3}	59.81	56.52
384	2	2.64×10^{-3}	59.65	56.62
392	2	3.63×10^{-3}	59.61	56.74
394	2	4.09×10^{-3}	59.59	56.63
401	4	5.92×10^{-3}	59.52	56.37
405	3	6.53×10^{-3}	59.51	56.60
407	2	7.10×10^{-3}	59.49	56.59
413	1	8.85×10^{-3}	59.41	56.63
415	2	1.01×10^{-2}	59.39	56.44
420	2	1.22×10^{-2}	59.37	56.46
424	1	1.29×10^{-2}	59.33	56.79
425	2	1.45×10^{-2}	59.30	56.48
430	2	1.71×10^{-2}	59.28	56.55
435	2	1.97×10^{-2}	59 26	56.68
440	2	2.24×10^{-2}	59.21	56.84
445	1	2.85×10^{-2}	59.20	56.60
			Average	56.56 ± 0.11

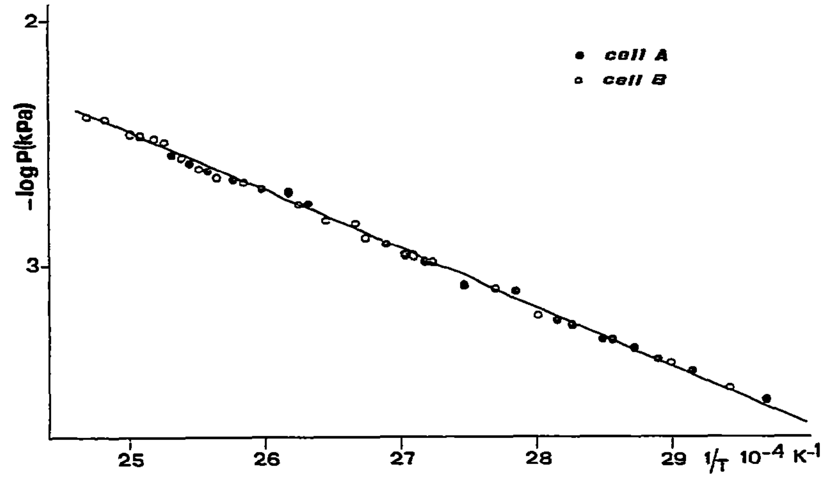

Fig. 1. Vapor pressure of $Al(acac)_3$.

thermocouples while gold—chromel thermocouples were used in the low temperature range. The instruments were tested using indium as calibrating substance. The measured C_p^0 values for indium were compared with those reported in the literature [9]. The data were found to be in agreement within ±1%. The experimental heat capacities of solid $Al(acac)_3$ and $Cu(acac)_2$ are summarized in Table 3.

Calculation of the thermodynamic functions

The thermodynamic functions of solid and gaseous compounds are reported in Table 4. They were evaluated for the solid phase employing the experimental heat capacities reported in Table 3 and for the gas phase on the

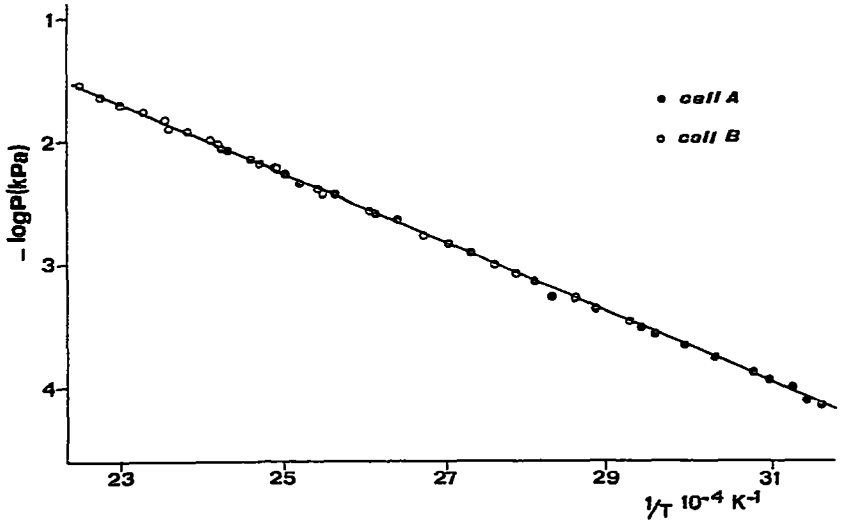

Fig. 2. Vapor pressure of $Cu(acac)_2$.

TABLE 3

Experimental heat capacity measurements

T (K)	C_p^0 * (J mole^{-1} K^{-1})	
	Al(acac)$_3$	Cu(acac)$_2$
4.2	0.13	0.09
5	0.19	0.12
7	0.42	0.27
10	0.76	0.49
15	1.70	1.09
20	3.02	1.94
25	4.72	3.03
30	6.80	3.47
35	9.26	5.95
40	12.10	7.77
50	18.90	12.14
60	27.22	17.48
70	37.04	23 79
80	48.38	31.07
90	61.23	39.33
100	75.60	48.55
120	108.86	69.91
145	158.95	102.08
150	170.10	109.24
175	231.50	148.68
180	244.94	157.30
190	272.92	175.30
200	302.20	194.19
225	307.09	199.11
240	310.00	202.02
250	312.05	203.95
275	316.90	208.88
298	321.4	213.4
300	321.8	213.8
325	326.7	218.7
350	331.6	223.6
375	336.5	228.5
400	341.4	233.5
425	346.3	238.3
450	351.2	243.2

* The C_p^0 measures are accurate within ±0.05 J mole^{-1} K^{-1} in the temperature range 4.2—275 K, and ±1.5 J mole^{-1} K^{-1} above 275 K.

basis of the available spectroscopic [10] and structural data [11—13] using the methods of statistical thermodynamics [14]. As regards the evaluation of the vibrational contribution, it was necessary to fill the knowledge of the IR data with the Raman and inactive frequencies. These modes were estimates according to the normal coordinate treatment [15] using the suitable sets of force constants [11,16—19] and the structural parameters [11—13]. The results of these calculations are summarized in Table 5. The electronic ground states were assumed as singlet for Al(acac)$_3$ and as triplet for Cu-

TABLE 4

Thermodynamic functions of Al(acac)$_3$ and Cu(acac)$_2$

Solid phase				Gas phase		
T (K)	S^0_T (J mole^{-1} K^{-1})	$-(G^0_T - H^0_{298})/T$ (J mole^{-1} K^{-1})	$(H^0_T - H^0_{298})$ (J mole^{-1})	S^0_T (J mole^{-1} K^{-1})	$-(G^0_T - H^0_{298})/T$ (J mole^{-1} K^{-1})	$(H^0_T - H^0_{298})$ (J mole^{-1})
Al(acac)$_3$						
298.15	479.0	479.0	0	502.48	502.48	0
300	480.4	479.2	384	504.00	502.97	309
325	500.5	481.3	6240	524.31	508.87	5017
350	520.5	483.5	12939	544.39	514.86	10334
375	540.2	489.9	18866	564.28	520.92	16260
400	559.9	496.4	25400	584.00	527.01	22794
425	579.3	502.7	32542	603.58	533.14	29937
450	598.6	509.0	40293	623.02	539.27	37689
Cu(acac)$_2$						
298.15	373.0	373.0	0	433.75	433.75	0
300	375.4	373.7	504	433.89	433.77	36
325	383.7	374.3	3046	438.36	434.41	1285
350	405.2	375.8	10290	459.19	436.06	8095
375	423.8	377.2	17471	477.71	439.21	14436
400	439.8	378.7	24452	492.99	442.26	20292
425	453.7	380.3	31182	507.64	447.36	25619
450	465.6	382.0	37611	520.00	452.27	30478
Associated error	±1.5	±1.5	±20	±0.05	±0.05	±15

TABLE 5

Calculated Raman and inactive frequencies (cm^{-1})

Al(acac)$_3$

A_1 *	A_2 ***	E **
ν(CH) 3090	ν(60) 185	ν(36) 195
ν(CO) 1575	ν(61) 120	ν(37) 170
ν(CC) 1225	ν(62) 50	ν(38) 115
ν(CR) 960		ν(39) 125
ν(AlO) 500		ν(40) 80
ν(ring) 650		ν(41) 45
δ(ring) 220		
δ(CH) 1195		
ν(ring) 225		
ν(ring) 215		
ν(ring) 380		

Cu(acac)$_2$

A_g *	A_u ***	B_{1g} *	B_{2u} **	B_{2g} *	B_3 *	B_{3u} **
ν(CH) 3090	ν(ring) 510	δ(CR) 440	ν(26) 105	ν(CH) 800	ν(CO) 1565	ν(33) 195
ν(CO) 1555	ν(ring) 400	ν(CR) 265		δ(ring) 255	ν(CC) 1530	ν(34) 125
ν(CC) 1285	ν(CR) 300			δ(ring) 220	ν(CR) 950	ν(35) 65
ν(CR) 825				δ(ring) 215	ν(CuO) 375	
ν(CuO) 485					δ(CH) 1195	
δ(ring) 645					δ(ring) 350	
δ(CR) 660					δ(ring) 235	
δ(ring) 230						

* Raman-active vibrations

** IR and Raman-active (A_2 and E) and IR-active (B_{2u} and B_{3u}) vibrations falling below 200 wavenumber and out of the range of the spectroscopic study reported in ref. 11. They are labelled according to the numbering in ref 19.

*** Inactive vibrations.

(acac)$_2$, the same as the Al^{3+} and Cu^{2+} ions. The errors associated with the thermodynamic functions of the solid phase are based on the uncertainty of the heat capacity measurements while those of the gas phase were estimated assuming an error of ±2° and ±0.1 Å for the bond angles and lengths, ±2 cm^{-1} and ±10 cm^{-1} for the measured and calculated frequencies, respectively.

CONCLUSIONS

Least squares treatment of the vapor pressure data yields the following equations given as weighted averages of the experimental measurements

Al(acac)$_3$ $\log P(\mathrm{kPa}) = 3.44 \pm 0.15 - (2359 \pm 48)/T$

Cu(acac)$_2$ $\log P(\mathrm{kPa}) = 4.80 \pm 0.15 - (2828 \pm 25)/T$

The associated errors are the standard deviations. From the slopes of these equations, the enthalpy changes ΔH_{371} (sub) = 45.2 ± 0.9 kJ mole^{-1} and ΔH_{380} (sub) = 54.1 ± 0.5 kJ mole^{-1} for Al(acac)$_3$ and Cu(acac)$_2$, respectively, were derived. These values were reported to 298 K using the heat content functions summarized in Table 4. The second-law ΔH^0_{298} sublimation heats, 47.7 ± 0.9 kJ mole^{-1} for Al(acac)$_3$ and 56.9 ± 0.5 kJ mole^{-1} for Cu(acac)$_2$, are in agreement with the corresponding third-law values, 46.5 ± 0.1 kJ mole^{-1} and 56.6 ± 0.1 kJ mole^{-1} (the errors are the standard deviations). On this basis we propose for the sublimation processes of the following ΔH^0_{298} values for the sublimation processes of Al(acac)$_3$ and Cu(acac)$_2$: 47 ± 1 kJ mole^{-1} and 57 ± 1 kJ mole^{-1}. The errors were estimated considering the uncertainties in the instrumental constants and in the temperature measurements. For Al(acac)$_3$ different sublimation enthalpy changes, namely 19.2, 66.3 and 23.4 kJ mole^{-1}, are reported in the literature [2,3,20]. Our proposed value, ΔH^0_{298} = 47 ± 1 kJ mole^{-1}, differs noticeably from these data. However, a comparison is not possible owing to the rather scarce number of measurements carried out in previous experiments [2,3,20] which prevented the derivation of a reliable second-law ΔH^0_{298}. In addition, no third-law calculations were made. In our case the relatively large number of experimental points, their reproducibility and the very good agreement between second- and third-law give support to the result proposed here.

ACKNOWLEDGMENT

We would like to express our gratitude to Prof. C. Balducci for helpful discussions and suggestions.

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