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STANDARD ENTHALPY OF FORMATION OF TRIS(2,4-PENTANEDIONATO)COBALT(III): THE MEAN (Co–O) BOND-DISSOCIATION ENTHALPY

MANUEL A.V. RIBEIRO DA SILVA, M. LUISA C.C.H. FERRÃO
and ARMINDA M.L. MAGALHÃES

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, 4000 Porto (Portugal)

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ABSTRACT

The standard enthalpy of formation of the crystalline complex of cobalt(III) with 2,4-pentanedione (HACAC) was determined, at 298.15 K, by solution–reaction calorimetry as -1233.9 ± 3.8 kJ mol^{-1}. The enthalpy of sublimation at 298.15 K, determined by microcalorimetry, was found to be 118 ± 5 kJ mol^{-1}.

The mean (Co–O) bond-dissociation enthalpy was derived as 165 ± 10 kJ mol^{-1}.

INTRODUCTION

The standard enthalpy of formation of Co(ACAC)$_3$ was determined in 1964 by Wood and Jones [1] from the enthalpy of combustion of the complex in oxygen. This early combustion study has been shown to have yielded unreliable results [2].

The solution–reaction calorimetric method has proved to be reliable for determining enthalpies of formation of metal β-diketonates [3] and was used previously for three cobalt(III) β-diketonates [4]. The present paper reports a redetermination of the standard enthalpy of formation of Co(ACAC)$_3$, using the solution–reaction calorimetric method.

EXPERIMENTAL

Materials

2,4-Pentanedione (HACAC) (BDH, AnalaR) was purified by fractional distillation and stored under nitrogen. Tris(2,4-pentanedionato)cobalt(III), Co(ACAC)$_3$, was prepared as described by Bryant and Fernelius [5] and purified by crystallization from (benzene + light petroleum). Microanalyses

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of $Co(ACAC)_3$: found: C, 50.54; H, 5.96; Co, 5.96%; expected: C, 50.57; H, 5.94; Co, 5.94%.

Cobalt(II) sulphate heptahydrate (BDH, AnalaR) was dried over silica gel; its composition was determined by means of cobalt analyses and found to be $CoSO_4 \cdot 6.00H_2O$. CERAC samples of $FeCl_2$ and $FeCl_3$ (stated minimum purity 99.99%), sulphuric and hydrochloric acids (BDH, AnalaR) were used. 1,4-Dioxan (Carl Erba) was purified by a reported method [6].

For the hydrolysis and oxidation reactions the solvents were degassed and saturated with purified nitrogen prior to each determination.

Solution–reaction calorimeter

The isoperibol LKB 8700 reaction-and-solution calorimeter was used. The operation and calculation methods have been reported [7]. The accuracy of the calorimeter was checked by measuring the molar enthalpy of solution of tris(hydroxymethyl)aminomethane (THAM) in aqueous 0.1000 mol dm^{-3} HCl, at 298.15 K: $\Delta_{sol}H_m = -29.769 \pm 0.024$ kJ mol^{-1}, in good agreement with the value of Kilday and Prosen [8], $\Delta_{sol}H_m = -29.770 \pm 0.032$ kJ mol^{-1}.

High-temperature microcalorimeter

The enthalpy of sublimation of $Co(ACAC)_3$ was measured by the "vacuum sublimation" drop-microcalorimetric method [9]. Samples (about 3 mg) of the complex contained in a small thin glass capillary tube sealed at one end, were dropped, at room temperature, into the hot reaction vessel in the Calvet high-temperature microcalorimeter held at 474 K, and then removed from the hot-zone by vacuum sublimation. At this temperature, the complex showed no signs of decomposition, and sublimed completely in less than 30 min. The observed molar enthalpy of sublimation $[H_m^\ominus(\text{g}, 474\ \text{K}) - H_m^\ominus(\text{cr}, 298.15\ \text{K})]$ was corrected to 298.15 K using values of $[H_m^\ominus(\text{g}, 474\ \text{K}) - H_m^\ominus(\text{g}, 298.15\ \text{K})]$ estimated by a group additivity scheme based on data given by Stull et al. [10]. The microcalorimeter was calibrated in situ for these measurements, by making use of the reported enthalpy of sublimation of naphthalene [10].

All uncertainty intervals are twice the standard deviation of the mean.

RESULTS

The thermochemical reaction for determining the standard molar enthalpy of formation of $Co(ACAC)_3$ was

$$Co(ACAC)_3(cr) + HCl \cdot 12.15H_2O(l) + H_2SO_4 \cdot 53.44H_2O(l) + FeCl_2(cr)$$
$$= 59.59H_2O(l) + FeCl_3(cr) + 3HACAC(l) + CoSO_4 \cdot 6.00H_2O(cr)$$

TABLE 1

Calorimetric study at 298.15 K of $Co(ACAC)_3$

(a) $HCl \cdot 12.15H_2O(l) + \text{solvent} = \text{solution } A_1$

$n \times 10^4$ (mol)	$(\Delta R/R_m) \times 10^4$	ε (J)	$\Delta_1 H_m$ (kJ mol^{-1})
2.4931	7.8792	6622.5	−20.930
2.5162	7.6795	6680.6	−20.389
2.4872	7.7284	6670.0	−20.725
2.4731	7.5256	6690.6	−20.359
2.5041	7.7162	6693.9	−20.627
Mean			−20.61 ± 0.21

(b) $H_2SO_4 \cdot 53.44H_2O(l) + \text{solution } A_1 = \text{solution } A_2$

$n \times 10^4$ (mol)	$(\Delta R/R_m) \times 10^3$	ε (J)	$\Delta_2 H_m$ (kJ mol^{-1})
2.4989	1.9495	6744.9	−52.621
2.4999	1.9542	6771.5	−52.935
2.5017	1.9632	6758.1	−53.034
2.5010	1.9711	6709.5	−52.879
2.4956	1.9363	6750.7	−52.377
Mean			−52.77 ± 0.24

(c) $Co(ACAC)_3(cr) + \text{solution } A_2 = \text{solution } A_3$

$n \times 10^4$ (mol)	$(\Delta R/R_m) \times 10^4$	ε (J)	$\Delta_3 H_m$ (kJ mol^{-1})
2.5156	−6.3870	6809.4	+17.289
2.5284	−6.7097	6685.4	+17.741
2.2690	−5.8207	6704.7	+17.200
2.5089	−6.4320	6775.8	+17.371
2.5089	−6.4329	6736.6	+17.273
Mean			+17.37 ± 0.19

(d) $FeCl_2(cr) + \text{solution } A_3 = \text{solution F}$

$n \times 10^4$ (mol)	$(\Delta R/R_m) \times 10^3$	ε (J)	$\Delta_4 H_m$ (kJ mol^{-1})
2.6303	2.1030	6806.3	−54.418
2.5001	2.0082	6815.3	−54.744
2.5664	2.0953	6688.9	−54.611
2.4528	2.0179	6658.6	−54.780
2.5538	2.0701	6778.5	−54.946
Mean			−54.70 ± 0.18

(e) $H_2O(l) + \text{solvent} = \text{solution } B_1$

$n \times 10^2$ (mol)	$(\Delta R/R_m) \times 10^3$	ε (J)	$\Delta_5 H_m$ (kJ mol^{-1})
1.4896	2.1141	6796.3	−0.9646
1.4866	2.1189	6782.0	−0.9667
1.4902	2.1185	6767.7	−0.9621
1.4901	2.1219	6782.0	−0.9658
1.4921	2.1390	6709.7	−0.9619
Mean			−0.964 ± 0.002

(continued)

TABLE 1 (continued)

(f) $FeCl_3(cr) + \text{solution } B_1 = \text{solution } B_2$

$n \times 10^4$ (mol)	$(\Delta R/R_m) \times 10^3$	ε (J)	$\Delta_6 H_m$ (kJ mol^{-1})
2.3495	2.8389	6770.2	−81.804
2.2915	2.7301	6759.1	−80.528
2.5930	3.1330	6746.6	−81.516
2.4814	2.9912	6734.9	−81.185
2.5800	3.1150	6753.0	−81.533
Mean			−81.31 ± 0.44

(g) $HACAC(l) + \text{solution } B_2 = \text{solution } B_3$

$n \times 10^4$ (mol)	$(\Delta R/R_m) \times 10^4$	ε (J)	$\Delta_7 H_m$ (kJ mol^{-1})
7.4643	−3.9318	6697.3	+3.528
7.4812	−3.9019	6718.3	+3.504
7.4653	−3.8208	6794.8	+3.478
7.4942	−3.8541	6730.9	+3.462
7.4753	−3.9431	6735.3	+3.553
Mean			+3.505 ± 0.032

(h) $CoSO_4 \cdot 6.00H_2O(cr) + \text{solution } B_3 = \text{solution F}$

$n \times 10^4$ (mol)	$(\Delta R/R_m) \times 10^3$	ε (J)	$\Delta_8 H_m$ (kJ mol^{-1})
2.4935	−1.3802	6713.0	+37.158
2.4924	−1.3932	6836.0	+38.212
2.4909	−1.3589	6914.0	+37.719
2.5008	−1.3549	6878.9	+37.269
2.4772	−1.3243	6836.0	+36.545
Mean			+37.38 ± 0.56

The initial calorimetric solvent was [0.75(1,4-dioxan) + 0.25HCl(aq, 4.2 mol dm^{-3})]. The reaction was studied in the presence of an excess of $FeCl_3$: to the calorimetric solvent (100.0 cm^3), 1.00 cm^3 of $FeCl_3$ 0.1 mol dm^{-3} was added. The standard enthalpy, $\Delta_r H_m^\ominus$, of the thermochemical reaction was determined by measuring the enthalpies of solution of stoichiometric amounts of reactants and products successively in the initial calorimetric solvent, so that the final solution resulting from dissolution of all the reactants was of the same composition as that from dissolution of all the products. The detailed calorimetric results required for determination of $\Delta_r H_m^\ominus$ are given in Table 1. They lead to

$$\Delta_r H_m^\ominus = \Delta_1 H_m + \Delta_2 H_m + \Delta_3 H_m + \Delta_4 H_m - 59.59\Delta_5 H_m - \Delta_6 H_m - 3\Delta_7 H_m - \Delta_8 H_m$$

$$= -19.85 \pm 0.84 \text{ kJ mol}^{-1}$$

With the following auxiliary data, $\Delta_f H_m^\ominus$(kJ mol^{-1}): $H_2O(l)$, −285.83 ± 0.04 [11]; HCl in $12.15H_2O(l)$, −162.23 ± 0.01 [12]; H_2SO_4 in $53.44H_2O(l)$, −886.86 ± 0.01 [12]; $FeCl_2(cr)$, −341.74 ± 0.21 [12,13]; $FeCl_3(cr)$, −399.49 ± 0.29 [12,13]; $CoSO_4 \cdot 6.00H_2O(cr)$, −2683.6 ± 2.1 [12]; HACAC(l),

TABLE 2

Enthalpy of sublimation of $Co(ACAC)_3$

Mass (mg)	T (K)	$\Delta_{sub}H(T)$ (kJ mol^{-1})	$\Delta_{sub}H_m^\ominus$(298.15 K) (kJ mol^{-1})
2.400	474	195.1	117.2
2.535	474	196.9	119.0

-425.5 ± 1.0 [14], we calculate the value $\Delta_f H_m^\ominus[Co(ACAC)_3, cr] = -1233.9 \pm 3.8$ kJ mol^{-1}.

Table 2 lists the experimental results for determining the enthalpy of sublimation of $Co(ACAC)_3$; the mean value at 298.15 K is $\Delta_{sub}H_m^\ominus = 118 \pm 5$ kJ mol^{-1}.

DISCUSSION

The standard enthalpy of formation of $Co(ACAC)_3$ reported in this paper differs considerably from that originally obtained from static-bomb combustion calorimetry. The original value -1364 ± 18 kJ mol^{-1} [1] differs from the reaction calorimetric value -1233.9 ± 3.8 kJ mol^{-1}, by 130 kJ mol^{-1}, demonstrating the unreliability of the combustion method applied to these complexes.

Table 3 lists the enthalpy of sublimation and the enthalpies of formation in the crystalline and gaseous states of the complex studied, together with the corresponding values for three other cobalt(III) β-diketonates, studied previously [4].

The mean cobalt–oxygen bond-dissociation enthalpy, $\langle D \rangle$(Co–O), in $Co(ACAC)_3$, may be defined as one sixth of the molar enthalpy of the disruption reaction, $\Delta_{disr}H_m^\ominus$

$$Co(ACAC)_3(g) \rightarrow Co(g) + 3ACAC(g)$$

To obtain $\Delta_f H_m^\ominus$(ACAC,g), the molar enthalpy of dissociation of the enolic hydrogen, D(O–H, HACAC, enol) in the enol form of HACAC is

TABLE 3

Molar values (kJ mol^{-1}) at 298.15 K

Complex	$\Delta_f H_m^\ominus$(cr)	$\Delta_{sub}H_m^\ominus$	$\Delta_f H_m^\ominus$(g)	$\langle D \rangle$(Co–O)
$Co(ACAC)_3$	-1233.9 ± 3.8	118 ± 5	-1115.9 ± 6.3	165 ± 10
$Co(BZAC)_3$ [a]	-877.2 ± 8.7	165 ± 10	-712 ± 13	164 ± 10
$Co(DPM)_3$ [a]	-1708 ± 12	126 ± 3	-1582 ± 12	171 ± 10
$Co(TFAC)_3$ [a]	-3191 ± 15	114 ± 2	-3077 ± 15	177 ± 10

[a] Reference 4.

required. Taking $D(\text{O–H, HACAC, enol}) = 418 \pm 20$ kJ mol^{-1} [3] and, with the following $\Delta_f H_m^\ominus$ values (kJ mol^{-1}): HACAC(enol, g), -384.4 ± 1.3 [14]; H(g), 218.00 ± 0.01 [11], we calculate $\Delta_f H_m^\ominus(\text{ACAC, g}) = -184 \pm 20$ kJ mol^{-1}. With $\Delta_f H_m^\ominus(\text{Co, g}) = 424.7 \pm 4.2$ kJ mol^{-1} [12], $\Delta_{\text{disr}} H_m^\ominus$ is calculated as 989 ± 60 kJ mol^{-1} and the mean cobalt-oxygen bond-dissociation enthalpy was derived (Table 3).

The values for the mean cobalt–oxygen bond-dissociation enthalpies $\langle D \rangle$(Co–O), in the four different cobalt(III) β-diketonates listed in Table 3, show that they are the same within the experimental uncertainties associated with them; these large uncertainties mainly arise from the uncertainty associated with the enthalpy of dissociation of the enolic hydrogen from the parent ligand. Under these circumstances, no effect upon $\langle D \rangle$(Co–O), or only a very small one, can be assigned to $-C_6H_5$, $-C(CH_3)_3$ or $-CF_3$ substitution in the ligand. This behaviour has been observed previously for complexes of β-diketones with Be(II) [15], Al(III) [15], Cr(III) [16], Fe(III) [17], Cu(II) [18,19], Co(II) [20] and Mn(III) [21].

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