THE ENTHALPIES OF FORMATION OF BIS-(BENZENE)MOLYBDENUM AND OF BIS-(TOLUENE)TUNGSTEN

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Summary

Microcalorimetric measurements at 520—523 K of the heats of thermal decomposition and of iodination of bis-(benzene)molybdenum and of bis-(toluene)tungsten have led to the values (kJ mol^{-1}): $\Delta H_f^0[\text{Mo}(\eta\text{-}C_6H_6)_2, c] = (235.3 \pm 8)$ and $\Delta H_f^0[\text{W}(\eta^6\text{-}C_7H_8)_2, c] = (242.2 \pm 8)$ for the standard enthalpies of formation at 25°C. The corresponding $\Delta H_f^0(g)$ values, using available and estimated enthalpies of sublimation, are (329.9 ± 11) and (352.2 ± 11) respectively, from which the metal—ligand mean bond-dissociation enthalpies, $\bar{D}(\text{Mo}—\text{benzene}) = (247.0 \pm 6)$ and $\bar{D}(\text{W}—\text{toluene}) = (304.0 \pm 6)$ kJ mol^{-1}, are derived.

1. Introduction

Although the enthalpies of formation of several bis-arene complexes of chromium have been reported [1], similar data are not available for bis-arene complexes of molybdenum or tungsten, apart from the measurement by Fischer and Reckzeigel [2] in 1961 of the energy of combustion of bis-(benzene)molybdenum. Microcalorimetric measurements at elevated temperatures have provided [3] values for the enthalpies of formation of three arene-tricarbonyl complexes of Mo and W, from which it was concluded that arene ligands bind more strongly to tungsten than to molybdenum. Similar microcalorimetric studies are now reported on bis-(benzene)molybdenum and bis-(toluene)tungsten.

2. Experimental

Calorimeter

The Calvet twin cell high temperature microcalorimeter (ambient to 1000°C), supplied by Setaram (Lyon), was adapted to the drop-microcalorimetric technique, as previously described [4]. The thermopile output was amplified (NV 724 A nanovoltmeter amplifier), and the thermograms recorded

(Rikadenki, DBE 2). The thermogram areas were simultaneously evaluated by the ITC integrator and printer. The calorimeter was calibrated from measurements of the enthalpy of sublimation of iodine, benzoic acid, and naphthalene.

Compounds

Samples of $[Mo(\eta\text{-}C_6H_6)_2]$ and $[W(\eta^6\text{-}C_6H_5CH_3)_2]$ were provided for these studies by Dr. M.L.H. Green (Oxford University). They were prepared by metal vapour synthesis [6].

3. Auxiliary data

All heat quantities are given in joules (J) or kilojoules (kJ). The following auxiliary heats for formation (kJ mol^{-1}) were used in evaluating the experimental results: $\Delta H_f^0(C_6H_6, g) = (82.88 \pm 0.52)$ [6]; $\Delta H_f^0(C_6H_5CH_3, g) = (50.17 \pm 0.42)$ [6]; $\Delta H_f^0(I_2, g) = (62.44 \pm 0.04)$ [7]; $\Delta H_f^0(MoI_3, c) = -(113.0 \pm 10.5)$ [8]; $\Delta H_f^0(WI_3, c) = -(46.0 \pm 12.5)$ [8]; $\Delta H_f^0(Mo, g) = (658.1 \pm 2.1)$ [9], and $\Delta H_f^0(W, g) = (859.9 \pm 4.6)$ [10]. To convert ΔH^T values to ΔH^{298}, $(H^T - H^{298})$ values for Mo and W metals were taken from the compilation of Hultgren et al. [11], and for benzene and toluene, from the data compilation of Stull, Westrum and Sinke [12].

4. Results

(i) Bis-(benzene)molybdenum [Mo(η-C₆H₆)₂]

Attempts to measure the enthalpy of sublimation of $[Mo(\eta\text{-}C_6H_6)_2]$ by the vacuum sublimation microcalorimetric technique [13] were made at $T = 395$ K and at 425 K, but were not successful, as thermal decomposition accompanied sublimation, and a metallic film formed in the exit tube from the reaction vessel.

Thermal decomposition in argon gas took place completely within the reaction vessel at 520 K. Molybdenum metal remained as a black powder within the capillary tube sample container, but also deposited as a bright mirror on the wall of the glass reaction bessel. The measured enthalpy of decomposition, $\Delta H_{dec.}^{520}$, refers to the cell process

$$[Mo(C_6H_6)_2, c, 298] \rightarrow Mo(c, 520) + 2\ C_6H_6(g, 520) \tag{1}$$

The reaction cell was evacuated when thermal decomposition was complete (return of the thermogram trace to the base-line), to remove benzene vapour from the system and ensure that the solid residue in the capillary container did not retain traces of undecomposed sample. Results are summarized in Table 1; Δh is the enthalpy change actually measured for each experiment in the microcalorimeter.

In other measurements, $[Mo(\eta\text{-}C_6H_6)_2]$ samples were dropped into iodine vapour contained in the reaction vessel at 520 K. The measured enthalpy, ΔH_{iod}^{520}, referes to the partial iodination reaction:

$$[Mo(C_6H_6)_2, c, 298] + \frac{n}{2} I_2(g, 520) \rightarrow MoI_n(c, 520) + 2\ C_6H_6(g, 520) \tag{2}$$

TABLE 1

THERMAL DECOMPOSITION OF $[Mo(\eta\text{-}C_6H_6)_2]$ AT 520 K [a]

Run	Sample mass (mg)	Δh (J)	ΔH_{dec}^{520} (kJ mol^{-1})
1	3.876	—0.3564	—23.2
2	2.890	—0.0432	—3.8
3	3.985	—0.1739	—11.0
4	3.365	—0.3661	—27.4
5	4.451	—0.0450	—2.6

Mean $\Delta H_{dec}^{520} = -(13.6 \pm 8)$ kJ mol^{-1}

$\Delta H_{dec}^{298} = -(69.9 \pm 8)$ kJ mol^{-1}

Benzene(g): $(H^{520} - H^{298}) = 25.38$ kJ mol^{-1}
Mo(c): $(H^{520} - H^{298}) = 5.54$ kJ mol^{-1}
$[Mo(C_6H_6)_2]$; M.W. = 252.17

[a] Error limits quoted are uncertainties = twice standard deviation of the mean.

Values of n were determined by analysis of the iodine content of the solid residue on removal of the reaction vessel from the calorimeter. The contribution to the measured heat of reaction from iodination of the metal made use of earlier measurements [8],

$$Mo(c, 539) + 1.38\ I_2(g, 539) \rightarrow MoI_{2.76}\ (c, 539); \Delta H_3 = -(189.95 \pm 8.4)\ kJ\ mol^{-1}$$

$$(3)$$
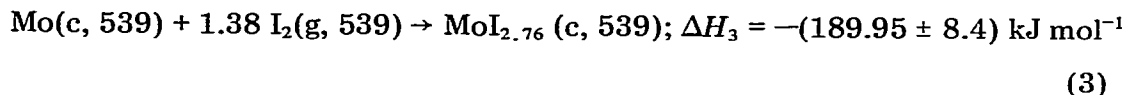
A contribution $(n/2.76 \times \Delta H_3)$ for formation of MoI_n, to ΔH_{iod}^{520} was accepted. Results are summarized in Table 2.

TABLE 2

IODINATION OF $[Mo(\eta\text{-}C_6H_6)_2]$ AT 520 K

Run	Sample mass (mg)	Δh (J)	n	ΔH_{iod}^{520} (kJ mol^{-1})	$\dfrac{n}{2.76}\Delta H_3$ (kJ mol^{-1})	ΔH_{dec}^{520} (kJ mol^{-1})
1	4.686	—1.080	0.65	—58.1	—44.8	—13.3
2	3.766	—0.6955	0.57	—46.6	—39.5	—7.1
3	5.767	—1.184	0.55	—51.8	—38.0	—13.8
4	4.926	—0.9547	0.46	—48.9	—31.9	—17.0
5	1.199	—0.451	1.05	—94.9	—72.2	—22.7

Mean $\Delta H_{dec}^{520} = -(14.8 \pm 6)$ kJ mol^{-1}

$\Delta H_{dec}^{298} = -(71.1 \pm 7)$ kJ mol^{-1}

(ii) Bis-(toluene)tungsten $[W(\eta^6\text{-}C_7H_8)_2]$

Thermal decomposition studies were made at 523 K. The measured enthalpy, ΔH_{dec}^{523} refers to the cell reaction,

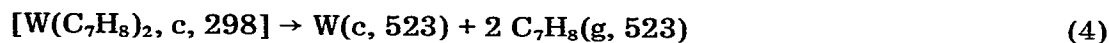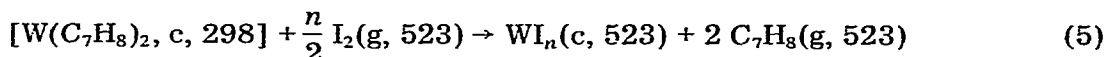$$[W(C_7H_8)_2, c, 298] \rightarrow W(c, 523) + 2\ C_7H_8(g, 523) \qquad (4)$$

TABLE 3

THERMAL DECOMPOSITION OF $[W(\eta^6\text{-}C_7H_8)_2]$ AT 523 K

Run	Sample mass (mg)	Δh (J)	$\Delta H_{\text{dec}}^{523}$ (kJ mol^{-1})
1	5.535	—0.9266	—61.6
2	4.130	—0.7830	—69.8
3	4.654	—0.9396	—74.3
4	3.742	—0.8348	—82.1
5	4.652	—1.0249	—81.1
6	4.187	—0.7247	—63.7

Mean $\Delta H_{\text{dec}}^{523}$ = —(72.1 ± 7) kJ mol^{-1}

Mean $\Delta H_{\text{dec}}^{298}$ = —(142.3 ± 7) kJ mol^{-1}

$C_6H_5CH_3$(g); $(H^{523} - H^{298})$ = 32.325 kJ mol^{-1}

W(c); $(H^{523} - H^{298})$ = 5.59 kJ mol^{-1}

$[W(C_7H_8)_2]$; M.W. = 368.133

and results are summarized in Table 3. Iodination measurements were also made at 523 K (Table 4). The values $\Delta H_{\text{iod}}^{523}$ refer to the reaction

$$[W(C_7H_8)_2, \text{c}, 298] + \frac{n}{2} I_2(\text{g}, 523) \rightarrow WI_n(\text{c}, 523) + 2 C_7H_8(\text{g}, 523) \qquad (5)$$

The contribution to $\Delta H_{\text{iod}}^{523}$ from iodination of tungsten metal was based on earlier measurements [8];

$$W(\text{c}, 530) + 1.37 I_2(\text{g}, 530) \rightarrow WI_{2.75}(\text{c}, 530); \Delta H_6 = -(126.36 \pm 11.3) \text{ kJ mol}^{-1} \qquad (6)$$
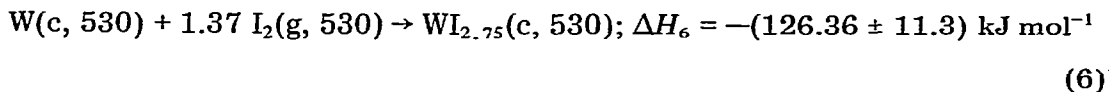
TABLE 4

IODINATION OF $[W(\eta^6\text{-}C_7H_8)_2]$ AT 523 K

Run	Sample mass (mg)	ΔH (J)	n	$\Delta H_{\text{iod}}^{523}$ (kJ mol^{-1})	$\dfrac{n}{2.75} \Delta H_6$ (kJ mol^{-1})	$\Delta H_{\text{dec}}^{523}$ (kJ mol^{-1})
1	4.245	—1.0206	0.263	—88.5	—12.1	—76.4
2	4.295	—0.9385	0.343	—80.4	—15.8	—64.6

Mean $\Delta H_{\text{dec}}^{523}$ = —(70.5 ± 6) kJ mol^{-1}

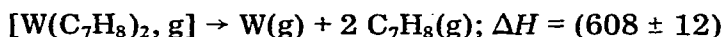Mean $\Delta H_{\text{dec}}^{298}$ = —(141.5 ± 7) kJ mol^{-1}.

Discussion

The average value, $\Delta H_{\text{dec}}^{298}$ = —(70.5 ± 7) kJ mol^{-1}, from thermal decomposition and iodination measurements on $[Mo(\eta\text{-}C_6H_6)_2]$ corresponds to $\Delta H_f^0[Mo\text{-}(C_6H_6)_2, \text{c}]$ = (253.3 ± 8) kJ mol^{-1}, and the average $\Delta H_{\text{dec}}^{298}$ for $[W(\eta\text{-}C_6H_5CH_3)_2]$ = —(141.9 ± 7) kJ mol^{-1}, corresponds to $\Delta H_f^0[W(C_6H_6CH_3)_2, \text{c}]$ = (242.2 ± 8) kJ mol^{-1}. Cox and Pilcher [6] quote a value, $\Delta H_{\text{sub}}^{298}$ = (94.6 ± 8) kJ mol^{-1} (based

on vapour pressure measurements by Fischer and Fritz [14]) for the enthalpy of sublimation of [Mo(η-C$_6$H$_6$)$_2$] at 25°C. The vapour pressure measurements (Knudsen cell) on bis-(benzene)tungsten by Fischer and Fritz, (later examined by Zorin, Umilin and Vanchagova [15]) over the range 10—40°C gave ΔH_{sub}^{298} ~ 106 kJ mol^{-1}. There are no available measurements on bis-(toluene)tungsten, and we accept a slightly higher value ΔH_{sub} ~ (110 ± 8) kJ mol^{-1} as a reasonable estimate.

These values lead to ΔH_f^0[Mo(η-C$_6$H$_6$)$_2$, g] = (329.9 ± 11) kJ mol^{-1}, and ΔH_f^0[W(η^6-C$_7$H$_8$)$_2$, g] = (352.2 ± 11) kJ mol^{-1}, from which the enthalpies of disruption:

$$[Mo(C_6H_6)_2, g] \rightarrow Mo(g) + 2 \ C_6H_6(g); \ \Delta H = (494 \pm 11)$$

and

$$[W(C_7H_8)_2, g] \rightarrow W(g) + 2 \ C_7H_8(g); \ \Delta H = (608 \pm 12)$$
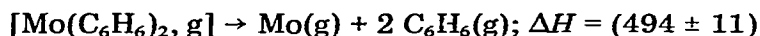
are derived, corresponding to mean bond-dissociation enthalpy values, $\bar{D}$[Mo—benzene] = (247 ± 6) kJ mol^{-1} and $\bar{D}$[W—toluene] = (304 ± 6) kJ mol^{-1}. For comparison, $\bar{D}$(Cr—benzene) in bis-(benzene)chromium [1] = (165 ± 5) kJ mol^{-1}.

Enthalpies of disruption, previously determined [3], of [(mesitylene)Mo-(CO)$_3$], [(hexamethylbenzene)Mo(CO)$_3$] and [(mesitylene)W(CO)$_3$] are (733 ± 15), (747 ± 12) and (879 ± 16) kJ mol^{-1}, respectively. In the hexacarbonyls, $\bar{D}$(Mo—CO) = 152 kJ mol^{-1}, $\bar{D}$(W—CO) = 180 kJ mol^{-1}, and transfer of these unchanged to the arenetricarbonyls leaves $\bar{D}$(Mo—mesitylene) ~ (279 ± 15), $\bar{D}$(Mo—hexamethylbenzene) ~ (291 ± 12) and $\bar{D}$(W—mesitylene) ~ (339 ± 16) kJ mol^{-1}. These are higher than the $\bar{D}$ values for (Mo—benzene) and (W—toluene) now reported - and in this respect resemble values similarly obtained for (Cr—mesitylene) and (Cr—hexamethylbenzene) in arenechromium tricarbonyls, when compared with (Cr—benzene) or (Cr—mesitylene) in the bis arenes of Cr. The transfer of $\bar{D}$(Cr—CO) unchanged from Cr(CO)$_6$ is questioned by Connor et al. [1], and it seems probable that similar objection applies to the transfer of $\bar{D}$(Mo—CO) and $\bar{D}$(W—CO) from hexacarbonyls to arene tricarbonyls of these elements.

Acknowledgements

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