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ENTHALPY OF FORMATION OF PENTACARBONYL(TRIPHENYLPHOSPHINE) TUNGSTEN AND OF PENTACARBONYL(METHOXY(PHENYL)-METHYLENE)TUNGSTEN

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Summary

Microcalorimetric studies on the sublimation, thermal decomposition and bromination of $W(CO)_6$, and of the complexes $[W(CO)_5(PPh_3)]$ and $[W(CO)_5\{C(OMe)Ph\}]$ have provided standard enthalpies of formation (in kJ mol^{-1}) of the crystalline and vapour states respectively as follows: $W(CO)_6$ $-(960 \pm 3)$, $-(887 \pm 4)$; $[W(CO)_5(PPh_3)]$ $-(729 \pm 7)$, $-(585 \pm 8)$; $[W(CO)_5\{C(OMe)Ph\}]$ $-(724 \pm 11)$, $-(620 \pm 12)$. The bond enthalpy contribution of the non-carbonyl ligand in these complexes is calculated; the results are consistent with some degree of double-bond character in the W–ligand bond.

Introduction

The enthalpy of formation of hexacarbonyltungsten is reasonably well-established from combustion calorimetry [1]. Enthalpies of formation have also been reported for $[W(CO)_3L_3]$ ($L_3 = C_6H_3Me_3$, C_7H_8 [2]; $(C_5H_5N)_3$, $(MeCN)_3$ [3]) obtained by microcalorimetric studies on these compounds. The results imply that the bond enthalpy contributions, $\bar{D}(W{-}NC_5H_5)$ and $\bar{D}(W{-}NCMe)$ in these complexes are of similar magnitude to (and slightly weaker than) $\bar{D}(W{-}CO)$ in $W(CO)_6$. In the present work, we report microcalorimetric studies on the thermal decomposition and bromination of monosubstituted derivatives of $W(CO)_6$ in which the substituents are triphenylphosphine and methoxy(phenyl)methylene. These measurements lead to values for the enthalpies of formation of the gaseous complexes, and the bond enthalpy contributions $D(W{-}PPh_3)$ and $D(W{=}C(OMe)Ph)$.

Experimental

Calorimeter. The Calvet high-temperature microcalorimeter (Setaram, Lyon) and the "drop" microcalorimetric technique have been described previously [4,5].

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Materials. Hexacarbonyltungsten was a commercial sample (Pressure Chemical, Pittsburg) which was purified by resublimation. The complexes $[W(CO)_5(PPh_3)]$ [6] and $[W(CO)_5\{C(OMe)Ph\}]$ [7] were prepared by standard methods. The purity of each complex was established by microanalysis and by spectroscopic measurements (IR, NMR, mass) which were in agreement with published values.

Auxiliary data. The following standard enthalpies of formation were used in evaluating the experimental results (values in kJ mol^{-1}): $CO(g) = -(110.524 \pm 0.17)$ [8]; $PPh_3(c) = (218 \pm 10.7)$ [9]; $PPh_3(g) = (314.2 \pm 13.6)$ [9]; $W(CO)_6(c) = -(960.2 \pm 3)$ [1]; $W(CO)_6(g) = -(887 \pm 5)$ [1,5]; $Br_2(g) = (30.907 \pm 0.11)$ [8]; $I_2(g) = (62.44 \pm 0.04)$ [8]; $WBr_5(c) = -(314.5 \pm 3.9)$ [10]; $WBr_6(c) = -(345.7 \pm 3.5)$ [10]; $Ph(MeO)C = C(OMe)Ph(g) \sim -(81 \pm 6)$ [*]; $W(g) = (859.9 \pm 4.6)$ [11]; $CH_2(g) = (390.4 \pm 4)$ [12]; $\{C(OMe)Ph\} = (323.7 \pm 5)$ [**].

Results

Enthalpies of sublimation

Measured enthalpies of sublimation of $[W(CO)_5PPh_3]$ and of $[W(CO)_5\text{-}\{C(OMe)Ph\}]$ are summarized in Table 1. The values ΔH_1^T refer to the following process (eq. 1)

$$[W(CO)_5L]\ (c, 298) \rightarrow [W(CO)_5L](g, T) \qquad (1)$$

The values ΔH_{sub}^{298} were obtained by subtraction of the heat content difference $(H_T - H_{298})$ of the vapour from ΔH_1^T; the latter was estimated assuming additivity in the sense $(H_T - H_{298}) \sim \Sigma(H_T - H_{298})$ for $L(g) + 5CO(g) + W(c)$.

Hexacarbonyltungsten

Thermal decomposition in argon gas was studied over the range 600–616 K.

TABLE 1

SUBLIMATION OF $[W(CO)_5(PPh_3)]$ AND $[W(CO)_5\{C(OMe)Ph\}]$

Compound	T (K)	Sample mass (mg)	ΔH_1^T (kJ mol^{-1})	ΔH_{sub}^{298} (kJ mol^{-1})
$[W(CO)_5(PPh_3)]$	431	1.999	206.5	140.5
	431	2.682	214.7	148.7
	431	2.705	208.3	142.3
	Mean $\Delta H_{sub}^{298} = (143.8 \pm 2.5)$ kJ mol^{-1}			
$[W(CO)_5\{C(OMe)Ph\}]$	380	2.619	130.7	103.9
	380	3.314	133.3	106.6
	380	3.091	128.9	102.1
	Mean $\Delta H_{sub}^{298} = (104.2 \pm 1.3)$ kJ mol^{-1}			

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[*] Estimated value, obtained from $\Delta H_f^\circ[PhCH{=}CHPh,g] = (234.9 \pm 3.4)$ kJ mol^{-1} [8] by adding twice the difference $[\Delta H_f^\circ(MeOCH{=}CH_2,g) - \Delta H_f^\circ(C_2H_4,g)]$, ~ -315.6 kJ mol^{-1}.

[**] Estimated value, assuming that the dissociation enthalpy, $C_2H_4 \rightarrow 2CH_2$, $\Delta H = (728.6 \pm 8)$ kJ mol^{-1} [13], also applies to $Ph(MeO)C{=}C(OMe)Ph \rightarrow 2[C(OMe)Ph]$.

TABLE 2

THERMAL DECOMPOSITION OF $[W(CO)_6]$

Sample mass (mg)	T (K)	ΔH_2^T (kJ mol^{-1})	ΔH_2^{298} (kJ mol^{-1})
2.710	616	362.4	297.8
2.055	616	365.1	300.5
2.659	616	351.5	286.9
2.388	616	374.6	309.9

Decomposition was incomplete at lower temperatures, but appeared to be complete at 616 K, giving a heavy mirror deposit on the walls of the reaction vessel, and in the capillary tube container. Results are summarized in Table 2, where ΔH_2^T refers to the hot-zone reaction (eq. 2).

$$[W(CO)_6](c, 298) \rightarrow W(c,T) + 6CO(g,T) \qquad (2)$$

The mean value, $\Delta H_2^{298} = (298.8 \pm 4.7)$ kJ mol^{-1} leads to $\Delta H_f^\circ[W(CO)_6,c] = -(961.8 \pm 9)$ kJ mol^{-1}, in fair agreement with that obtained (-960.3 kJ mol^{-1}) from combustion measurements [1].

The bromination of $W(CO)_6$ was studied at 426 K, by dropping samples into excess bromine vapour in the hot reaction vessel. Reaction was rapid, leaving a black powder residue; capillary sample containers, open at both ends, proved advantageous in these measurements. The ΔH_3^T values (Table 3) refer to the cell-reaction (eq. 3).

$$[W(CO)_6](c, 298) + \frac{n}{2}Br_2(g,T) \rightarrow WBr_n(c,T) + 6CO(g,T) \qquad (3)$$

Values of n in WBr_n were determined from bromine analysis of the solid residues. The derived mean value $\Delta H_f^\circ[W(CO)_6,c] = -(962.0 \pm 6)$ kJ mol^{-1} is in fair agreement with those given earlier.

Pentacarbonyl(triphenylphosphine)tungsten

Thermal decomposition at 616 K gave a metallic mirror on the walls of the reaction vessel, leaving a metal powder residue within the shiny capillary tube sample containers. A white film (triphenylphosphine) condensed on cooler parts of

TABLE 3

BROMINATION OF $[W(CO)_6]$

Sample mass (mg)	T (K)	ΔH_3^T (kJ mol^{-1})	n	ΔH_3^{298} (kJ mol^{-1})	ΔH_f°(c) (kJ mol^{-1})
2.561	426	−72.5	5.16	−104.4	−957.7
2.585	426	−66.1	5.27	−98.2	−969.1
2.371	426	−75.5	5.34	−107.7	−963.0
2.211	426	−66.9	5.25	−98.9	−967.5
2.510	426	−72.7	5.05	−104.4	−952.7

TABLE 4

THERMAL DECOMPOSITION OF [W(CO)$_5$(PPh$_3$)]

Sample mass (mg)	T (K)	ΔH_4^T (kJ mol^{-1})	ΔH_4^{298} (kJ mol^{-1})
2.328	616	673.9	494.5
2.044	616	669.0	489.6
2.054	616	663.4	484.0
2.141	616	680.4	501.0
2.138	616	662.3	482.8

the exit tube. The measured enthalpies, ΔH_4^T, refer to the hot-zone reaction, (eq. 4),

$$[\mathrm{W(CO)_5(PPh_3)}](\mathrm{c}, 298) \rightarrow \mathrm{W}(\mathrm{c}, T) + 5\mathrm{CO}(\mathrm{g}, T) + \mathrm{PPh_3}(\mathrm{g}, T) \tag{4}$$

and are summarized in Table 4.

The mean value $\Delta H_4^{298} = (490.4 \pm 3.4)$ kJ mol^{-1}, corresponds to ΔH_f° [[W(CO)$_5$(PPh$_3$)],c] $= -(728.8 \pm 7)$ kJ mol^{-1}; the quoted error limits do not include uncertainty in the accepted value of ΔH_f°[PPh$_3$,c].

Bromination studies were made at temperatures in the range 417–425 K. The measured heats include the exothermic contribution from bromination of the triphenylphosphine ligand, which was evaluated separately by dropping triphenylphosphine samples into bromine/argon in the hot-zone at 420–423 K. Results are summarized in Table 5. On combining these results, eq. 5a, and eq. 5b,

$$[\mathrm{W(CO)_5(PPh_3)}](\mathrm{c},298) + \text{excess } \mathrm{Br_2}(\mathrm{g},T) \rightarrow$$
$$\mathrm{WBr}_n(\mathrm{c},T) + 5\mathrm{CO}(\mathrm{g},T) + \{\mathrm{PPh_3/Br_2},T\} \tag{5a}$$

$$\mathrm{PPh_3}(\mathrm{c},298) + \text{excess } \mathrm{Br_2}(\mathrm{g},T) \rightarrow \{\mathrm{PPh_3/Br_2},T\} \tag{5b}$$

we obtain, eq. 5c

$$[\mathrm{W(CO)_5(PPh_3)}](\mathrm{c},298) + \frac{n}{2}\mathrm{Br_2}(\mathrm{g},T) \rightarrow \mathrm{PPh_3}(\mathrm{c},298) +$$
$$5\mathrm{CO}(\mathrm{g},T) + \mathrm{WBr}_n(\mathrm{c},T) \tag{5c}$$

TABLE 5

BROMINATION OF Ph$_3$P AND [W(CO)$_5$(PPh$_3$)]

Compound	Sample mass (mg)	T (K)	ΔH^T (kJ mol^{-1})
Ph$_3$P	2.056	420	−184.4
	1.867	421	−170.2
	3.088	423	−177.0
	Mean value = −(177.2±4) kJ mol^{-1})		
[W(CO)$_5$(PPh$_3$)]	2.439	417	−187.1
	2.729	425	−173.9
	2.458	425	−197.9
	2.259	425	−171.5
	Mean value = −(182.6±6) kJ mol^{-1}		

TABLE 6

THERMAL DECOMPOSITION OF $[W(CO)_5\{C(OMe)\{Ph\}]$

Sample mass (mg)	T (K)	ΔH_6^T (kJ mol^{-1})	ΔH_6^{298} (kJ mol^{-1})
3.070	593	226.7	120.6
2.911	603	238.4	128.3
1.519	603	231.9	121.8
1.855	603	252.3	142.2
1.988	603	252.4	142.3

with $\Delta H \sim -(5.4 \pm 7)$ kJ mol^{-1}. The value of n in these experiments was not determined. For $n = 5.5$, ΔH_{5c}^{298} isothermal at 298 K, adjusts to $\sim -(34 \pm 7)$ kJ mol^{-1}, leading to $\Delta H_f^\circ[[W(CO)_5(PPh_3),c] \sim -(716 \pm 8)$ kJ mol^{-1}. For $n = 6$, the derived ΔH_f° becomes -738 kJ mol^{-1}, and represents the upper exothermal limit.

Pentacarbonyl(methoxy(phenyl)methylene)tungsten

Thermal decomposition in argon gas was studied in the temperature range 593–603 K; a bright mirror formed on the walls of the reaction vessel, and a black powder remained in the capillary tube container. A thin white film settled out in the cooler exit tube. The results are summarized in Table 6, and are interpreted on the basis of the presumed decomposition [13] (eq. 6).

$$[W(CO)_5\{C(OMe)Ph\}](c,298) \rightarrow W(c,T) + 5CO(g,T) + Ph(MeO)C{=}C(OMe)Ph(g,T) \qquad (6)$$

The mean value $\Delta H_6^{298} = (131 \pm 5)$ kJ mol^{-1} leads to ΔH_f° $[W(CO)_5\{C(OMe)Ph\}],c] = -(724 \pm 11)$ kJ mol^{-1}.

Discussion

The thermochemical results from the present and from earlier studies on tungsten carbonyl complexes are collected in Table 7, which gives derived enthalpies of formation, $\Delta H_f^\circ(c)$, heats of sublimation, ΔH_{sub}, and enthalpies of formation in the gaseous state, $\Delta H_f^\circ(g)$. The enthalpy of disruption, $\Delta H_{disrupt}$ for the dissociation reactions (eq. 7a,b), can be calculated from $\Delta H_f^\circ(g)$ values. Transfer of the mean

$$[W(CO)_5L,g] \rightarrow W(g) + 5CO(g) + L(g) \qquad (7a)$$

$$[W(CO)_3L_3,g] \rightarrow W(g) + 3CO(g) + 3L(g) \qquad (7b)$$

bond dissociation enthalpy, $\bar{D}(W{-}CO) = (180.7 \pm 1)$ kJ mol^{-1} in $W(CO)_6$ [1], to the various complexes provides the bond enthalpy contributions, $\bar{D}(W{-}L)$. The use of a pulsed laser pyrolysis technique has provided a measure of the first bond dissociation energy in $W(CO)_6$, $D([(OC)_5W{-}CO]) = (192.5 \pm 8.4)$ kJ mol^{-1} [14], so that $\Delta H_f^\circ[W(CO)_5,g] = -(584 \pm 13)$ kJ mol^{-1}. The dissociation energies of W–L bonds in $[W(CO)_5L]$ complexes $D([OC)_5W{-}L])$ have been calculated, eq. 8,

$$[W(CO)_5L,g] \rightarrow [W(CO)_5,g] + L(g) \qquad (8)$$

The results of both approaches are shown in Table 7.

TABLE 7

ENTHALPIES OF FORMATION AND BOND ENTHALPIES IN CARBONYLTUNGSTEN DERIVATIVES

Compound	ΔH_f°(c)	Ref.	ΔH_{sub}°	Ref.	ΔH_f°(g)	$\Delta H_{disrupt}$	$\bar{D}$(W–L)	L	D((OC)$_5$W–L)
W(CO)$_6$	−960 ± 3	1	73.2 ± 1	5	−887 ± 4	1084 ± 6	180.7 ± 1	CO	192.5 ± 8
[W(CO)$_5$(PPh$_3$)]	−729 ± 7	[a]	143.8 ± 2.5	[a]	−585 ± 8	1207 ± 9	303 ± 10	PPh$_3$	315 ± 13
[W(CO)$_5${C(OMe)Ph}]	−724 ± 11	[a]	104.2 ± 1.3	[a]	−620 ± 12	1251 ± 14	348 ± 15	C(OMe)Ph	356 ± 16
[W(CO)$_5$(C$_5$H$_{11}$N)]	−922	[b]	106.4 ± 1.0	[c]	−815	1066	173	[d]	182
[W(CO)$_5$(C$_5$H$_5$N)]	−716	[b]	109.7 ± 2.7	[c]	−606	1044	151	[e]	163
[W(CO)$_3$(C$_5$H$_5$N)$_3$]	−250 ± 12	3	~146	3	−104 ± 20	1066 ± 21	175 ± 7	[e]	–
[W(CO)$_3$(NCMe)$_3$]	−405 ± 12	3	~96	3	−309 ± 20	1054 ± 21	171 ± 7	[f]	–
[W(CO)$_3$(η-C$_6$H$_3$Me$_3$)]	−477 ± 13	2	111 ± 6	2	−366 ± 15	879 ± 16	337 ± 16	[g]	–

[a] This work. [b] H. Daamen, H. van der Poel, D.J. Stufkens, and A Oskam, Thermochim. Acta, 34 (1979) 69. [c] H. Daamen, J.M. Ernsting and A. Oskam, Thermochim. Acta, 33 (1979) 217. [d] Piperidine. [e] Pyridine. [f] Acetonitrile. [g] 1,3,5-Trimethylbenzene.

The order of W–L bond enthalpy contributions indicates that a phosphine ligand (PPh_3) forms a stronger bond to tungsten(0) than do a range of nitrogen donor ligands. This matches a similar pattern in $[PtCl_2L_2]$ complexes [15]. The enthalpy contribution of the carbenoid ligand D(W–C(OMe)Ph) is much greater than $\bar{D}(W{-}CH_3)$ both in WMe_6 (159 ± 7 kJ mol^{-1}) [16] and in $[W(\eta\text{-}C_5H_5)_2Me_2]$ (198 ± 8 kJ mol^{-1}) [17], which is consistent with the presence of partial double bond character in the W–C(OMe)Ph bond in the carbenoid complex. In agreement with this, the carbenoid (sp^2) C–W bond length (2.13 Å) in $[W(CO)_5(CPh_2)]$ [18] is shorter than the alkyl (sp^3) C–W bond length (2.26 Å) in $[W(dmpe)(CH_2Bu^t)(CHBu^t)(CBu^t)]$ but longer than the alkylidyne (C(sp)–W) bond length (1.94 Å) in the same molecule [19].

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