Enthalpies of Formation of Molybdenum and Tungsten Tri-iodides

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The enthalpies of reaction of $Mo(CO)_6$ and of $W(CO)_6$ with iodine vapour at temperatures in the range 520—540 K to form the tri-iodides of the metals have been measured with a Calvet high-temperature microcalorimeter. The results lead to $\Delta H_f^{\circ}(MoI_3,c) = -113 \pm 10$ kJ mol^{-1} $\cong$ $-27{\cdot}0 \pm 2{\cdot}5$ kcal mol^{-1} and $\Delta H_f^{\circ}(WI_3,c) = -46 \pm 13$ kJ mol^{-1} $\cong$ $-11{\cdot}0 \pm 3$ kcal mol^{-1} for the standard enthalpies of formation at 298 K.

EXPERIMENTAL data are completely lacking on the enthalpies of formation of the iodides of molybdenum and tungsten, and although estimates of these quantities have been made [1,2] there is little accord between them. The values now reported for $\Delta H_f^{\circ}(MoI_3,c)$ and for $\Delta H_f^{\circ}(WI_3,c)$ were derived from direct measurements of the enthalpies of iodination of the hexacarbonyls of Mo and W at elevated temperatures, a Calvet high-temperature microcalorimeter being used for this purpose. These iodinations were first examined in detail by Djordjevic, Nyholm, Pande, and Stiddard.[3] The derivation of the enthalpies of formation of the tri-iodides of Mo and W from the measured enthalpies of reaction requires prior knowledge of the enthalpies of formation

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[1] L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, 'Chemistry and Metallurgy of Miscellaneous Materials,' ed. L. L. Quill, McGraw-Hill, New York, 1950.

[2] R. C. Feber, U.S. Atomic Energy Comm., L.A.-3164, 1965.

[3] C. Djordjevic, R. S. Nyholm, C. S. Pande, and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1966, 16.

of $Mo(CO)_6$ and $W(CO)_6$ both of which have recently been redetermined.[4–6]

EXPERIMENTAL

Compounds.—Commercial samples of $Mo(CO)_6$ and $W(CO)_6$ supplied by R. N. Emanuel Ltd. and Strem Chemicals Inc. were purified before use by fractional sublimation *in vacuo*.

Calorimeter.—The high-temperature Calvet microcalorimeter (Setaram, Lyon), and its usage as a ' drop ' calorimeter for studies both of the thermal decomposition and the reaction with iodine of metal carbonyls has been described.[7–9] It was calibrated by dropping a capillary tube containing a weighed amount (*ca.* 10—15 mg) of crystalline iodine into the ' live ' cell of the microcalorimeter at the same time as an identical, but empty, glass capillary tube was dropped into the twin ' reference ' cell. The resulting thermogram area was measured, and related to the known enthalpy change[10] for the live-cell process $I_2(c,T_1) \longrightarrow I_2(g,T_2)$ where T_2 = calorimeter temperature, and T_1 = arrival temperature of the I_2 sample on reaching the hot zone of the calorimeter. About 30 min after the iodine ' drop,' a second capillary tube containing a weighed amount of metal carbonyl was dropped into the live cell (now containing I_2 and Ar), and simultaneously an identical but empty capillary was let fall into the twin reference cell. The recorded thermogram from this second drop refers to the iodination reaction, the extent of which was determined after the calorimeter experiment by (i) analysis of unchanged iodine remaining in the reaction vessel, and (ii) analysis of the iodine content of the black powder (metal iodide) formed. (The iodides of Mo and W are readily oxidized on being heated in oxygen to form MoO_3 or WO_3 liberating the iodine).

Auxiliary Quantities.—Enthalpy changes (Δh, ΔH) and enthalpies of formation ($\Delta H_f°$) are given in thermochemical calories, 1 cal = 4·1840 J. The following standard enthalpies of formation were accepted (values in kcal mol^{-1}): $\Delta H_f°(CO,g)$[1] = −26·416; $\Delta H_f°[Mo(CO)_6,c]$[5,6] = −236·5 ± 0·5; $\Delta H_f°[W(CO)_6,c]$[5,6] = −229·0 ± 0·8; and $\Delta H_f°(I_2,g)$[11] = +14·92.

RESULTS

Reaction of $Mo(CO)_6$ *with* I_2.—Measurements were made at T_2 = 539 K, with sample weights of 2·5—2·7 mg $Mo(CO)_6$. The reaction with I_2 vapour took place entirely within the reaction vessel, the inlet tube remaining clean. The black powder formed analysed as MoI_n, with n = 2·7—2·8. Results are summarized in Table 1.

TABLE 1

Iodination of $Mo(CO)_6$ at 539 K

Expt.	$Mo(CO)_6$/mg	I_2/mg	Δh/cal	n	ΔH_1/kcal mol^{-1}
1	2·490	14·255	0·428	2·80	45·$_7$
2	2·700	14·095	0·438	2·75	43·$_1$
3	2·730	14·130	0·436	2·73	42·$_4$
4	2·420	14·475	0·414	2·80	45·$_4$
5	2·480	14·260	0·420	2·70	45·$_0$

Mean n = 2·76. Mean ΔH_1 = 44·$_3$ kcal mol^{-1}.

The column Δh gives the measured enthalpy change in each calorimetric experiment, as determined from the recorded thermogram area. The values ΔH_1 refer to the process (1) the *mean* relating to process (2). The overall

$$Mo(CO)_6(c, 298) + \frac{n}{2}I_2(g, 539) \longrightarrow MoI_n(c, 539) + 6CO(g, 539) \quad (1)$$

$$Mo(CO)_6(c, 298) + 1{\cdot}38I_2(g, 539) \longrightarrow MoI_{2\cdot76}(c, 539) + 6CO(g, 539) \quad (2)$$

uncertainty in the mean ΔH_1, account being taken of the spread in calibration and experimental results, and the uncertainty in determining n, is estimated to be ±2 kcal mol^{-1}.

The value here accepted for $\Delta H_f°[Mo(CO)_6,c]$ requires that $\Delta H_3 = 78{\cdot}0 \pm 0{\cdot}5$ kcal mol^{-1} for the isothermal decomposition (3). For the non-isothermal decomposition

$$Mo(CO)_6(c, 298) \longrightarrow Mo(c, 298) + 6CO(g, 298) \quad (3)$$

(4) ΔH_4 is calculated to be 89·7 ± 0·5 kcal mol^{-1}, use being

$$Mo(CO)_6(c, 298) \longrightarrow Mo(c, 539) + 6CO(g, 539) \quad (4)$$

made of tabulated ($H_T - H_{298}$) data[10] for CO(g) and Mo(c). Combination of equations (2) and (4) gives $\Delta H_5 = \Delta H_1 - \Delta H_4 = -45{\cdot}4 \pm 2$ kcal mol^{-1} for the iodination reaction (5).

$$Mo(c, 539) + 1{\cdot}38I_2(g, 539) \longrightarrow MoI_{2\cdot76}(c, 539) \quad (5)$$

Estimates of ΔC_p for similar reactions to (5) have been made by Brewer *et al.*[1] on the basis of which ΔH_5 at 539 K becomes *ca.* −46·$_4$ ± 2 kcal mol^{-1} for the same reaction at 298 K. This leads to the value $\Delta H_f°(MoI_{2\cdot76},c)$ = −25·$_8$ ± 2 kcal mol^{-1}.

Reaction of $W(CO)_6$ *with* I_2.—Measurements were made over the temperature range 524—533 K with sample weights of 3—7 mg $W(CO)_6$. The product was a black powder, analysing as WI_n (n = 2·7—2·8). Results are summarized in Table 2. The mean ΔH_6 value refers to reaction (6). The overall uncertainty in the mean ΔH_6

TABLE 2

Iodination of $W(CO)_6$

Expt.	T_2/K	$W(CO)_6$/mg	I_2/mg	Δh/cal	n	ΔH_6/kcal mol^{-1}
1	524	2·915	14·545	0·410	2·70	49·$_8$
2	524	6·470	13·780	0·975	2·75	53·$_3$
3	533	4·135	15·515	0·690	2·70	56·$_6$
4	533	4·030	13·955	0·573	2·80	50·$_3$
5	533	3·882	13·870	0·548	2·80	50·$_0$

Mean T_2 = 530 K. Mean n = 2·75. Mean ΔH_6 = 52·0 kcal mol^{-1}.

$$W(CO)_6(c, 298) + 1{\cdot}37I_2(g, 530) \longrightarrow WI_{2\cdot75}(c, 530) + 6CO(g, 530) \quad (6)$$

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[4] D. S. Barnes, G. Pilcher, D. A. Pittam, H. A. Skinner, D. Todd, and Y. Virmani, International Conference on Chemistry and Uses of Molybdenum, University of Reading, Sept. 1973.

[5] G. Pilcher and D. A. Pittam, to be published.

[6] D. S. Barnes, G. Pilcher, H. A. Skinner, and D. Todd, to be published.

[7] H. A. Skinner and Y. Virmani, *Rev. Roumaine Chim.*, 1972, **17**, 467.

[8] J. A. Connor, H. A. Skinner, and Y. Virmani, *J.C.S. Faraday I*, 1972, 1754.

[9] J. A. Connor, H. A. Skinner, and Y. Virmani, *J.C.S. Faraday I*, 1972, 1218.

[10] D. R. Stull and H. Prophet, JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Govt. Printing Office, Washington D.C., June 1971.

[11] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, NBS Technical Note 270-4, U.S. Govt. Printing Office, Washington D.C., May 1969.

value is estimated at $\pm 2{\cdot}5$ kcal mol^{-1}. The value[5,6] $\Delta H_f°[W(CO)_6,c] = -229{\cdot}_0 \pm 0{\cdot}_8$ kcal mol^{-1} places $\Delta H_7 = 71{\cdot}0 \pm 0{\cdot}_8$ kcal mol^{-1} for the isothermal decomposition process (7). For the non-isothermal decomposition process

$$W(CO)_6(c, 298) \longrightarrow W(c, 298) + 6CO(g, 298) \quad (7)$$

(8), ΔH_8 is calculated to be $82{\cdot}_2 \pm 0{\cdot}_8$ kcal mol^{-1} using

$$W(CO)_6(c, 298) \longrightarrow W(c), 530) + 6CO(g, 530) \quad (8)$$

$(H_T - H_{298})$ tabulated data[10] for W(c) and CO(g). The combination of equations (6) and (8) leads to $\Delta H_9 = -30{\cdot}_2 \pm 2{\cdot}_7$ kcal mol^{-1} for the iodination reaction (9) which

$$W(c, 530) + 1{\cdot}37I_2(g, 530) \longrightarrow WI_{2\cdot 75}(c, 530) \quad (9)$$

becomes *ca.* $-31{\cdot}2 \pm 3$ kcal mol^{-1} for the same process at 298 K. The latter corresponds to $\Delta H_f°(WI_{2\cdot 75},c) = -10{\cdot}7 \pm 3$ kcal mol^{-1}.

DISCUSSION

Presuming the product $MoI_{2\cdot 76}$ to be a mixture of MoI_3 and MoI_2, we can write $\Delta H_f°(MoI_{2\cdot 76})$ in the equivalent form $\{0{\cdot}24\Delta H_f°(MoI_2) + 0{\cdot}76\Delta H_f°(MoI_3)\}$. The estimates of Brewer *et al.*[1] and of Feber[2] gave $\Delta H_{10} = -1{\cdot}5 \pm 1$ kcal mol^{-1} for reaction (10) from

$$MoI_2(c) + \tfrac{1}{2}I_2(c) \longrightarrow MoI_3(c) \quad (10)$$

which $\Delta H_f°(MoI_3,c) = \Delta H_f°(MoI_2,c) - 1{\cdot}5 \pm 1$ kcal mol^{-1}. By combining the latter with the measured value, $\Delta H_f°(MoI_{2\cdot 76},c) = -25{\cdot}_8 \pm 2$ kcal mol^{-1}, we obtain $\Delta H_f°(MoI_3,c) = -26{\cdot}_2 \pm 2$ and $\Delta H_f°(MoI_2,c) = -24{\cdot}_7 \pm 2{\cdot}_2$ kcal mol^{-1} respectively.

Feber has estimated that reaction (11) is virtually

$$WI_2(c) + \tfrac{1}{2}I_2(c) \longrightarrow WI_3(c) \quad (11)$$

thermoneutral, so that $\Delta H_f°(WI_3,c) = \Delta H_f°(WI_2,c)$. In this event and the product $WI_{2\cdot 75}$ being presumed to be a mixture of WI_3 and WI_2, the measured value, $-10{\cdot}_7 \pm 3$ kcal mol^{-1}, for $\Delta H_f°(WI_{2\cdot 75},c)$ applies equally to $\Delta H_f°(WI_3,c)$ and to $\Delta H_f°(WI_2,c)$. The assumption that the products $MoI_{2\cdot 76}$ and $WI_{2\cdot 75}$ were made up exclusively of admixtures of di-iodides with tri-iodides is invalid, since traces of free metal deposit were observed within the capillary tube containers. The alternative, but extreme, assumption that the products consisted exclusively of tri-iodides admixed with free metal leads to values of $-28{\cdot}_0$ and $-11{\cdot}_6$ kcal mol^{-1} respectively for $\Delta H_f°(MoI_3,c)$ and $\Delta H_f°(WI_3,c)$. Making an arbitrary allowance for the slight admixture of metal with the metallic iodides, we adopt $\Delta H_f°(MoI_3,c) = -27{\cdot}0 \pm 2{\cdot}_5$ kcal mol^{-1}, and $\Delta H_f°(WI_3,c) = -11{\cdot}_0 \pm 3$ kcal mol^{-1} as the best values from the present studies.

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