Enthalpies of Formation of the Pentafluorides and Oxide Tetrafluorides of Molybdenum and Tungsten

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The enthalpies of (oxidative) alkaline hydrolysis of the pentafluorides and of the oxotetrafluorides of molybdenum and of tungsten have been measured. From these values the respective enthalpies of formation of these compounds have been estimated to be $\Delta H_f^{\ominus}[MoF_5(c)] = -1387$; $\Delta H_f^{\ominus}[WF_5(c)] = -1457$; $\Delta H_f^{\ominus}[MoOF_4(c)] = -1380$; and $\Delta H^{\ominus}_f[WOF_4(c)] = -1500$ kJ mol^{-1}.

DATA are available on the enthalpies of formation of a number of higher chlorides, bromides, and iodides of transition metals, and of a few oxide chlorides and oxide bromides, but corresponding information about fluorides and oxide fluorides is very restricted. The enthalpies of formation of MoF_6,[1,2] WF_6,[2-4] and NbF_5 [2,5] have been estimated from fluorine bomb calorimetry [1,3-5] and from hydrolysis measurements,[2] those of TaF_5 [5] and RuF_5 [6] from fluorine bomb calorimetry alone, and those of VF_5 [7] and ReF_6 [8] from hydrolysis measurements only. A value is given, without a method, for IrF_6.[9] Thermochemical results have been reported for most compounds in the MOX_4 and MO_2X_2 series, where M = Mo or W, and X = Cl,[10,11] Br,[11,12] or I.[13] For X = F thermochemical data are available for WOF_4, for which an enthalpy of formation has been estimated by mass spectrometry.[14] Enthalpies of formation have also been estimated for MoO_2F_2 and WO_2F_2 from mass spectrophotometric experiments,[14] but there seems to be no certain report of the isolation and characterisation of WO_2F_2.† However, the preparation of WO_2F_2,2DMSO [15] and of WO_2F_2,2MeOH [16] has been claimed, and there is a suggestion that the dioxodifluorides may be produced in systems containing the trioxides and hydrogen fluoride.[17] It has been proposed, from extrapolations from available thermochemical data, that WO_2F_2 may be a major constituent in tungsten–fluoride incandescent lamps at high temperatures.[18]

In this paper we report measurements of the enthalpies of (oxidative) alkaline hydrolysis of the pentafluorides and of the oxotetrafluorides of molybdenum and tungsten, from which we have estimated values for the respective enthalpies of formation of these compounds.

EXPERIMENTAL

Preparations.—Tungsten pentafluoride was prepared by the reduction of tungsten hexafluoride over heated tungsten wires, using the apparatus described by Schröder and Grewe.[19] Molybdenum pentafluoride was prepared by an analogous method,[20] and by the established procedure of reducing molybdenum hexafluoride with molybdenum powder at 570—670 K.[21] Tungsten and molybdenum oxotetrafluorides were prepared by oxyfluorination of the respective powdered metals.[22] They were purified by vacuum sublimation at about 370 K. Products were analysed for tungsten by precipitation of the cinchonine–tannin complex and its ignition to tungsten(VI) oxide;[23] for molybdenum gravimetrically as its oxinate MoO_2-

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† Early workers in this area characterised MoO_2F_2 (O. Ruff and F. Eisner, *Chem. Ber.*, 1907, **40**, 2931), but were unable to isolate WO_2F_2 (O. Ruff, F. Eisner, and W. Heller, *Z. anorg. Chem.*, 1907, **52**, 256).

[1] J. L. Settle, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.*, 1961, **65**, 1337.

[2] O. E. Myers and A. P. Brady, *J. Phys. Chem.*, 1960, **64**, 591.

[3] P. A. G. O'Hare and W. N. Hubbard, *J. Phys. Chem.*, 1966, **70**, 3353.

[4] J. Schröder and F. Sieben, *Chem. Ber.*, 1970, **103**, 76.

[5] E. Greenberg, C. A. Natler, and W. N. Hubbard, *J. Phys. Chem.*, 1965, **69**, 2089.

[6] H. A. Porte, E. Greenberg, and W. N. Hubbard, *J. Phys. Chem.*, 1965, **69**, 2308.

[7] R. L. Cavell and H. C. Clark, *Trans. Faraday Soc.*, 1963, **59**, 2706.

[8] J. Burgess, C. J. W. Fraser, I. Haigh, and R. D. Peacock, *J.C.S. Dalton*, 1973, 501.

[9] Nat. Bur. Stand., Technical Note 270/4, 1969.

[10] S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvurov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, *Russ. J. Inorg. Chem.*, 1960, **5**, 802; H. Oppermann, *Z. anorg. Chem.*, 1971, **383**, 1.

[11] H. Oppermann, *Z. anorg. Chem.*, 1970, **379**, 262.

[12] S. A. Shchukarev and G. A. Kokovin, *Russ. J. Inorg. Chem.*, 1964, **9**, 849; H. Oppermann and G. Stover, *Z. anorg. Chem.*, 1971, **383**, 14.

[13] J. Tillack, *Z. anorg. Chem.*, 1968, **357**, 11; H. Oppermann, *ibid.*, 1971, **383**, 285.

[14] K. F. Zmbov, O. M. Uy, and J. L. Margrave, *J. Phys. Chem.*, 1969, **73**, 3008; K. F. Zmbov and J. L. Margrave, personal communication cited in JANAF Thermochemical Tables, 1971.

[15] R. Kergoat and J. E. Guerchais, *Bull. Soc. chim. France*, 1970, 2932.

[16] Y. A. Buslaev, S. P. Petrosyants, and V. I. Chagin, *Russ. J. Inorg. Chem.*, 1972, **17**, 368.

[17] L. G. Koshechko, E. G. Rakov, B. V. Gromov, B. N. Sudarikov, and L. A. Morozova, *Russ. J. Phys. Chem.*, 1971, **45**, 1071.

[18] G. M. Neumann, 4th European Symposium on Fluorine Chemistry, Ljubljana, 1972.

[19] J. Schröder and F. J. Grewe, *Chem. Ber.*, 1970, **103**, 1536; *Angew. Chem. Internat. Edn.*, 1968, **7**, 132.

[20] W. E. Falconer, G. R. Jones, W. A. Sunder, I. Haigh, and R. D. Peacock, *J. Inorg. Nuclear Chem.*, 1973, **35**, 751.

[21] A. J. Edwards, R. D. Peacock, and R. W. H. Small, *J. Chem. Soc.*, 1962, 4486.

[22] G. H. Cady and G. B. Hargreaves, *J. Chem. Soc.*, 1961, 1568.

[23] D. A. Lambie, *Analyst*, 1945, **70**, 124.

(oxine)$_2$;[24,25] and for fluoride by the fluorosilicic acid distillation method.[24,26]

Hydrolysis Reactions.—The molybdenum(VI) and tungsten(VI) compounds hydrolyse smoothly and swiftly in 1M or 0·1M NaOH:

$$e.g.\ MoF_6 + 8OH^- \longrightarrow MoO_4^{2-} + 6F^- + 4H_2O$$

The pentafluorides likewise hydrolyse in sodium hydroxide solution containing sodium hypochlorite:

$$e.g.\ 2MoF_5 + 14OH^- + ClO^- \longrightarrow 2MoO_4^{2-} + 10F^- + Cl^- + 7H_2O$$

Calorimetry.—The calorimeter consisted of a Dewar flask, thermostatted at 298·2 K, fitted with a heater (constantan wire) and a thermistor. Heats of reaction were measured by breaking a bulb containing a known mass (between 0·04 and 0·27 g) of compound under sodium hydroxide solution (1M or 0·1M; 150 cm^3) (for MoF$_6$, WF$_6$, MoOF$_4$, WOF$_4$) or sodium hydroxide (1M or 0·1M; 120 cm^3) plus sodium hypochlorite solution (10—12%; 30 cm^3) (for MoF$_5$, WF$_5$) and monitoring the temperature change with a Kipp BD 2 or Kipp–Zonen BD 5 recorder incorporated in the Wheatstone bridge containing the thermistor. The recorder deflections were calibrated by dissipating a known amount of energy in the heater. The performance of the calorimeter was checked periodically either by silver chloride precipitation[27] or by dissolution of tris(hydroxymethyl)methylamine in 0·1M HCl.[28]

RESULTS

Measured heats of hydrolysis are reported in Table 1. From these results and supplementary literature values,* enthalpies of formation of the hexafluorides, pentafluorides, and oxotetrafluorides of molybdenum and of tungsten have been calculated. Our results are reported, and where relevant compared with published values, in Table 2.

TABLE 1

Enthalpies of (oxidative) hydrolysis (ΔH_{hydr}) of the hexafluorides, pentafluorides, and oxotetrafluorides of molybdenum and of tungsten

Compound	No. of samples	Total no. hydrolyses	Mean ΔH_{hydr}/ kJ mol^{-1}	σ [a] /kJ mol^{-1}
MoF$_6$(g)	3	4	−732	4
WF$_6$(g)	2	4	−652	6
MoF$_5$(c)	6	6	−692	6
WF$_5$(c)	3	3	−701	8
MoOF$_4$(c)	3	4	−425	5
WOF$_4$(c)	3	10	−364	9

[a] The standard error of the mean ΔH_{hydr} and confidence limits at any required level may be calculated from the given standard deviation, σ, by standard methods (see, *e.g.*, E. S. Swinbourne, ' Analysis of Kinetic Data,' Nelson, London, 1971, pp. 7—9).

The four independent determinations of $\Delta H_f^\ominus$[WF$_6$(g)] in Table 2 show extremely good agreement; our value for $\Delta H_f^\ominus$[MoF$_6$(g)] is much closer to that obtained by fluorine bomb calorimetry than that derived from an earlier hydrolysis investigation. Our value for $\Delta H_f^\ominus$[WF$_5$(c)] agrees within experimental error with the earlier determination by fluorine bomb calorimetry; for WOF$_4$ there is a puzzling discrepancy between the two published $\Delta H_f^\ominus$ values from one group of workers, with our hydrolysis derived value agreeing with the earlier of their two estimates.

TABLE 2

Enthalpies of formation ($\Delta H_f^\ominus$) of the hexafluorides, pentafluorides, and oxotetrafluorides of molybdenum and tungsten

	This work	Published data		
Compound	$\Delta H_f^\ominus$/kJ mol^{-1}	$\Delta H_f^\ominus$/kJ mol^{-1}	Method	Ref.
MoF$_6$(g)	−1564	−1621	Hydrolysis	2
		−1558	Fluorine bomb	1
WF$_6$(g)	−1723	−1720	Hydrolysis	2
		−1722	Fluorine bomb	3
		−1723	Fluorine bomb	4
MoF$_5$(c)	−1387			
WF$_5$(c)	−1457	−1448	Fluorine bomb	4
MoOF$_4$(c)	−1380			
WOF$_4$(c)	−1500	−1391 or −1485 [a]	Mass spec.	14

[a] $\Delta H_f^\ominus$[WOF$_4$(c)] calculated from reported $\Delta H_f^\ominus$[WOF$_4$(g)] values using a value of 69 kJ mol^{-1} for the enthalpy of sublimation of WOF$_4$.

DISCUSSION

Tungsten pentafluoride has been prepared recently by Schröder, through the reduction of WF$_6$ at low pressures on a heated tungsten wire.[19] It is the least stable of the known pentafluorides and the heat of formation is in line with this, indicating, if reasonable entropy assumptions are made, its instability towards WF$_6$ and W metal (*cf.* ref. 29). The heat of formation of MoF$_5$ indicates the greater stability of this compound towards decomposition to the hexafluoride and the elements. For the reaction

$$6WF_{5(c)} = 5WF_{6(g)} + W_{(c)}$$

the enthalpy change, at 25 °C, is −100 kJ mol^{-1}; for the reaction

$$6MoF_{5(c)} = 5MoF_{6(g)} + Mo_{(c)}$$

it is +280 kJ mol^{-1}. Since the heat of the reaction MF$_{5(c)}$(polymer) $\longrightarrow$ MF$_{5(g)}$(monomer) is not known precisely for MoF$_5$ and for WF$_5$, it is not yet possible to estimate mean bond energies for these compounds.

From the heats of formation of MoOF$_4$ and WOF$_4$ more conclusions may be drawn, since it is known that these compounds vaporise directly to a monomeric gas. If the average metal–fluorine bond energy is assumed to be the same as in the hexafluorides, then metal–oxygen bond energies of 739 kJ mol^{-1} in MoOF$_{4(g)}$ and of 815 kJ mol^{-1} in WOF$_{4(g)}$ may be estimated (Table 3). The latter compares with a value of 776 kJ mol^{-1} in WOCl$_{4(g)}$. If these average values for bond strengths are used to

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* Standard enthalpies of formation have been taken from the National Bureau of Standards Technical Notes 270/3 [F$^-$(aq), Cl$^-$(aq), OH$^-$(aq), and H$_2$O(l)] and 270/4 [WO$_4^{2-}$(aq)]; from J. E. McDonald, J. P. King, and J. W. Cobble, *J. Phys. Chem.*, 1960, **64**, 1345 [ClO$^-$(aq)]; and R. L. Graham and L. G. Hepler, *J. Amer. Chem. Soc.*, 1956, **78**, 4846 [MoO$_4^{2-}$(aq)].

[24] A. I. Vogel, ' Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961.

[25] G. B. Hargreaves, Ph.D. Thesis, University of London, 1959.

[26] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Analyt. Edn.*, 1933, **5**, 7; F. Seel, *Angew. Chem. Internat. Edn.*, 1964, **3**, 424.

[27] E. Lange and R. M. Fuoss, *Z. phys. Chem.*, 1927, **125**, 431; G. J. Ewing and C. J. Mazac, *Analyt. Chem.*, 1966, **38**, 1575.

[28] R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, 1964, **18**, 195; J. O. Hill, G. Ojelund, and I. Wadsö, *J. Chem. Thermodynamics*, 1969, **1**, 111.

[29] J. Burgess, C. J. W. Fraser, R. D. Peacock, P. Taylor, A. Majid, and J. M. Winfield, *J. Fluorine Chem.*, 1973, **3**, 55.

TABLE 3

Enthalpies of formation of hexafluorides and of oxotetrahalides of tungsten and molybdenum from the respective atoms (ΔH_a), and average bond dissociation energies ($\bar{D}$) in these molecules

Compound	$-\Delta H_a$/ kJ mol^{-1}	$\bar{D}$(M–X)/ kJ mol^{-1}	$\bar{D}$(M–O)/ kJ mol^{-1}
WF_6(g)	3048	508	
MoF_6(g)	2692	449	
WOF_4(g)	2846 [a]	508	815
$MoOF_4$(g)	2535 [b]	449	739
$WOCl_4$(g)	2171 [c]	349	776

[a] Enthalpy of sublimation 69 kJ mol^{-1} (G. H. Cady and G. B. Hargreaves, *J. Chem. Soc.*, 1961, 1568). [b] Enthalpy of sublimation assumed to be 69 kJ mol^{-1}. [c] Enthalpy of formation of $WOCl_4$(g) = − 586 kJ mol^{-1} (N.B.S. Technical Note 270/4, 1969).

estimate the heats of formation of the gaseous dioxide difluorides MoO_2F_2 and WO_2F_2, then it appears that although MoO_2F_2 is predicted to be stable, WO_2F_2 is predicted to be unstable with respect to disproportionation into $WOF_{4(g)}$ and $WO_{3(c)}$. Several attempts to prepare WO_2F_2, for example by the interaction of WO_3 and WOF_4 under a variety of conditions, have so far been unsuccessful.[30] It is interesting to contrast the stabilities of the tungsten oxide fluorides with those of a typical *sp*-block element such as selenium, for which SeO_2F_2 is well established but $SeOF_4$ apparently as yet uncharacterised.

Enthalpies of formation of 'ternary' tungsten–chloride–fluoride and tungsten–methoxide–fluoride compounds have recently been determined.[29] From these results it proved possible to rationalise in thermochemical terms the respective redistribution and decomposition patterns characteristic of these two series of compounds. Our very limited information on the tungsten–oxide–fluoride series suggests a similarity to the tungsten–chloride–fluoride series.

Knowledge of the enthalpies of formation of these pentafluorides and oxotetrafluorides is not only of intrinsic interest but is also useful in the estimation of other thermochemical parameters of chemical interest. In particular these enthalpies of formation are required in thermochemical cycles used for estimating fluoride ion affinities of fluorine containing compounds. We have recently estimated fluoride ion affinities of a range of pentafluorides, including MoF_5 and WF_5, from thermochemical measurements on alkali metal salts of the respective MF_6^- anions;[31] we hope similarly to estimate fluoride ion affinities of MOF_4, M = Mo or W, from thermochemical measurements on salts of the MOF_5^- anions.

We thank Dr. J. Schröder for the loan of apparatus, the S.R.C. for the award of a C.A.P.S. (to I. H.), and Thorn Lighting Limited for discussions.

[3/1775 *Received*, 24*th August*, 1973]

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[30] J. Burgess, R. D. Peacock, and P. Taylor, unpublished observations (1973).

[31] J. Burgess, I. Haigh, and R. D. Peacock, *Chem. Comm.*, 1971, 977; J. Burgess, I. Haigh, P. Taylor, and R. D. Peacock, following paper.