ENTHALPIES OF FORMATION OF CHLORIDE FLUORIDES AND OF METHOXIDE FLUORIDES OF TUNGSTEN(VI)

J. BURGESS, C. J. W. FRASER, R. D. PEACOCK AND P. TAYLOR

Department of Chemistry, University of Leicester, Leicester LE1 7RH (Gt. Britain)

A. MAJID AND J. M. WINFIELD

Chemistry Department, University of Glasgow, Glasgow W.2. (Gt. Britain)
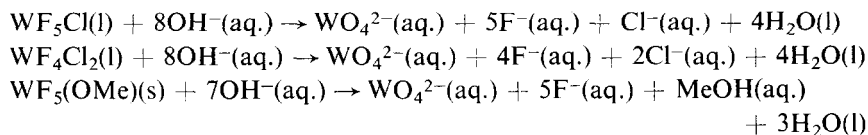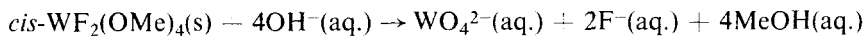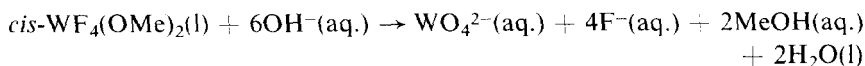
SUMMARY

Enthalpies of formation of the tungsten(VI) compounds WF_5Cl, WF_4Cl_2, $WF_5(OMe)$, *cis*-$WF_4(OMe)_2$ and *cis*-$WF_2(OMe)_4$ are reported. Re-distribution and decomposition reactions in the chloride–fluoride and in the methoxide–fluoride series are discussed in the light of the thermochemical results.

INTRODUCTION

Enthalpies of formation of several binary compounds of tungsten have been determined; two examples relevant to the present paper are tungsten hexafluoride [1] and tungsten hexachloride [2]. We are interested in determining enthalpies of formation of mixed compounds of tungsten(VI) of the type WA_xB_{6-x}, for example where A $=$ Cl and B $=$ F [3,4] and where A $=$ OMe and B $=$ F [5-7], to provide basic chemical information on these compounds and to provide some thermodynamic basis for discussions of their reactions. In this paper we report the determination of enthalpies of alkaline hydrolysis of some tungsten(VI) compounds of the type specified above. The compounds studied and the respective equations and stoichiometries for alkaline hydrolysis are:

$$WF_5Cl(l) + 8OH^-(aq.) \rightarrow WO_4^{2-}(aq.) + 5F^-(aq.) + Cl^-(aq.) + 4H_2O(l)$$

$$WF_4Cl_2(l) + 8OH^-(aq.) \rightarrow WO_4^{2-}(aq.) + 4F^-(aq.) + 2Cl^-(aq.) + 4H_2O(l)$$

$$WF_5(OMe)(s) + 7OH^-(aq.) \rightarrow WO_4^{2-}(aq.) + 5F^-(aq.) + MeOH(aq.) + 3H_2O(l)$$

$$cis\text{-}WF_4(OMe)_2(l) + 6OH^-(aq.) \rightarrow WO_4{}^{2-}(aq.) + 4F^-(aq.) + 2MeOH(aq.)$$
$$+ 2H_2O(l)$$
$$cis\text{-}WF_2(OMe)_4(s) + 4OH^-(aq.) \rightarrow WO_4{}^{2-}(aq.) + 2F^-(aq.) + 4MeOH(aq.)$$

From our measured enthalpies of alkaline hydrolysis and the known enthalpies of formation of hydroxide ion and of the reaction products in aqueous solution, the respective enthalpies of formation of the tungsten(VI) compounds have been estimated. The known decomposition and re-distribution reactions in the chloride–fluoride and methoxide–fluoride series are discussed in the light of these determined enthalpies of formation and the enthalpies of likely decomposition reactions.

EXPERIMENTAL

Preparations

Samples of tungsten chloride pentafluoride[3], *cis*- and *trans*-tungsten dichloride tetrafluoride[4], tungsten methoxide pentafluoride[5], *cis*-tungsten dimethoxide tetrafluoride[6] and *cis*-tungsten tetramethoxide difluoride[6] were prepared by the respective published methods. Their purity was assessed by analysis and by ^{19}F NMR spectroscopy. Samples were kept refrigerated between their preparation and use in subsequent thermochemical experiments to avoid significant decomposition.

Thermochemistry

A frangible glass bulb containing a known amount of compound was broken into an aqueous solution of 0.1 *M* sodium hydroxide solution contained in a glass Dewar vessel fitted with a stirrer, a Constantin wire heater for calibration purposes and a thermistor; this whole apparatus was held at constant temperature (25.0°) in a thermostatted tank. Changes in temperature of the contents of the Dewar flask were reflected in changes in thermistor resistance. The resistance of the thermistor was monitored by a Kipp BD-2 or a Kipp–Zonen BD-5 recorder incorporated in a Wheatstone bridge circuit.

RESULTS

Our experimental results, namely mean values for the enthalpies of alkaline hydrolysis of each compound, together with an indication of the precision of the result and the number of samples and hydrolyses in each case, are reported in Table 1. Also included in Table 1 are the enthalpies of formation of the compounds calculated from the respective enthalpies of hydrolysis and the literature data on enthalpies of formation listed in Table 2. The errors quoted for the enthalpies of formation have been estimated from the confidence limits of the enthalpies of hydrolysis plus a subjective allowance for systematic errors. These latter concern

experimental difficulties and compound purity; in some cases, an allowance has to be made for a (very small) amount of sample decomposition taking place during the equilibration time preceding thermochemical measurements. The enthalpy of solution of methanol in 0.1 M NaOH has been measured; it is 0.6 kcal mole^{-1}. This value has been used at the appropriate stage in the calculations of the enthalpies of formation of the methoxide complexes.

TABLE 1

ENTHALPIES OF HYDROLYSIS AND OF FORMATION

Compound	No. of samples	Total no. of hydrolyses	Mean enthalpy of hydrolysis[a] (kcal mole^{-1})	Enthalpy of formation[b] (kcal mole^{-1})	Enthalpy of formation (kJ mole^{-1})
$WF_5Cl(l)$	3	6	—147.0 ± 1.6	—391 ± 3	1640
$WF_4Cl_2(l)$[c]	3	6	—144.7 ± 0.4	—353 ± 3	1480
$WF_5(OMe)(s)$	3	17	—113.7 ± 1.4	—418 ± 3	1750
cis-$WF_4(OMe)_2(l)$	2	6	—91.4 ± 2.3	—405 ± 4	1690
cis-$WF_2(OMe)_4(s)$	1	3	—61.3 ± 0.4	—363 ± 4	1520

[a] Errors quoted in this column represent the 90 % confidence limits of the cited mean.
[b] Estimated errors as described in the text.
[c] Stereochemistry discussed in the text.

TABLE 2

THERMOCHEMICAL DATA USED IN CALCULATIONS OF ENTHALPIES OF FORMATION

Species	Standard enthalpy of formation (kcal mole^{-1})	Reference
$WO_4^{2-}(aq.)$	—257.1	8
$OH^-(aq.)$	—54.97	9
$F^-(aq.)$	—79.50	9
$Cl^-(aq.)$	—39.952	9
$H_2O(l)$	—68.315	9
$CH_3OH(l)$	—57.02	10

As all the published data which we have used are in units of kcal mole^{-1}, we have worked in these units; in Table 1 we have converted the final results into SI units in conformance with current British usage.

Preparations of tungsten dichloride tetrafluoride result in the formation of approximately 1:1 equilibrium mixtures of the *cis* and *trans* isomers which it has not so far proved possible to resolve into the components[4]. We have therefore only been able to determine the enthalpy of hydrolysis, and thence the enthalpy

of formation, of the equilibrium mixture. However it is known that the composition of the equilibrium mixture is not sensitive to temperature, which observation indicates that the enthalpy of the isomerisation reaction

$$cis\text{-WCl}_2\text{F}_4 \rightleftharpoons trans\text{-WCl}_2\text{F}_4$$
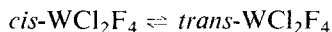
is very small. This in turn means that the values of $\Delta H_f^\circ(cis\text{-WCl}_2\text{F}_4)$ and of $\Delta H_f^\circ(trans\text{-WCl}_2\text{F}_4)$ are very nearly equal. The enthalpy of formation of -353 ± 4 kcal mole^{-1} given in Table 1 thus refers to the equilibrium mixture of *cis*- and *trans*-WF$_4$Cl$_2$.

DISCUSSION

The characteristic reaction pattern of tungsten chloride fluorides is of re-distribution, but that of tungsten methoxide fluorides is of decomposition, with elimination of the methyl group as some simple organic compound: *e.g.*

$$\text{WF}_5\text{OMe} \rightarrow \text{WOF}_4 + \text{MeF}$$
$$\text{WF}_4(\text{OMe})_2 \rightarrow \text{WOF}_4 + \text{Me}_2\text{O}$$
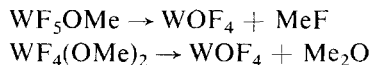
It is of interest to try to estimate enthalpies of re-distribution and of decomposition for members of the two series, to see how these reflect the established chemical behaviour.

Enthalpies of re-distribution can be estimated from the enthalpies of formation of the "ternary" compounds reported above and from the known enthalpies of formation of such compounds as tungsten hexafluoride (-412 kcal mole^{-1} (ref. 1)). Thus, for the reorganisation of tungsten methoxide pentafluoride:

$$2\text{WF}_5\text{OMe}(s) \rightarrow \text{WF}_6(g) + \text{WF}_4(\text{OMe})_2(l)$$
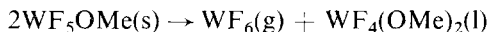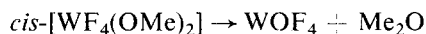
the enthalpy of reaction will be approximately $+20$ kcal mole^{-1}; for other likely re-distribution reactions in the methoxide–fluoride series, estimated enthalpies of re-distribution are significantly positive. These positive enthalpies of re-distribution suggest, even allowing for a small temperature–entropy product term, positive free energies of re-distribution. On the other hand, the enthalpy of decomposition of WF$_5$OMe to tungsten oxotetrafluoride and methyl fluoride is estimated as $+2$ kcal mole^{-1}, but indeed could be zero or very slightly negative within experimental uncertainty; a favourable entropy–temperature product (from the formation of gaseous methyl fluoride) indicates a negative free energy for this decomposition.

For the dimethoxide tetrafluoride the pattern is similar, with an estimated enthalpy of re-distribution to, for instance, the tetramethoxide difluoride and tungsten hexachloride

$$2cis\text{-}[\text{WF}_4(\text{OMe})_2](l) \rightarrow cis\text{-}[\text{WF}_2(\text{OMe})_4](s) + \text{WF}_6(g)$$
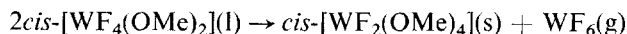
of $+30$ kcal per two moles of cis-$[WF_4(OMe)_2]$, but the estimated enthalpy for the decomposition*

$$cis\text{-}[WF_4(OMe)_2] \rightarrow WOF_4 + Me_2O$$

is -2 kcal mole^{-1}. Similarly, the enthalpy change for the reaction

$$3WF_4(OMe)_2 \rightarrow 2WF_5(OMe) + WF_2(OMe)_4$$
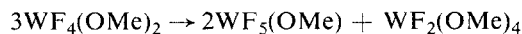
can be estimated as approximately $+16$ kcal mole^{-1}, and indeed this reaction is known to proceed in the opposite direction (right → left) at room temperature in hexafluorobenzene[7].

Possible decomposition reactions of the chloride fluorides, which are reductive in nature in contrast to the decomposition reactions cited above for methoxide fluorides, are:

$$WF_5Cl(l) \rightarrow WF_5(s) + \tfrac{1}{2}Cl_2(g) \qquad (1)$$

$$WF_5Cl(l) \rightarrow WF_4(s) + ClF(g) \qquad (2)$$

$$WF_4Cl_2(l) \rightarrow WF_4(s) + Cl_2(g) \qquad (3)$$
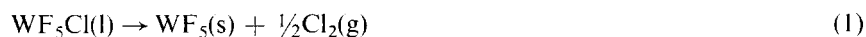
Mixed chloride fluorides of tungsten(V) or of tungsten(IV) seem less likely decomposition products as such compounds have not yet been reported. The enthalpy of formation of WF_5 is known—it is -346 kcal mole^{-1} for the solid[1]— but that of WF_4 is not known. However a reasonable estimate of this can be made from the inference that the disproportionation of WF_5 into WF_4 and WF_6 [11] goes to a position of equilibrium rather than to completion at room temperature. One can therefore assume that the free energy change for the reaction

$$2WF_5(s) \rightarrow WF_4(s) + WF_6(g)$$

is zero, to within 2–3 kcal mole^{-1}. From this assumption, estimated entropies** of 35 cal deg^{-1} mole^{-1} for $WF_4(s)$, 40 for $WF_5(s)$ and 84 for $WF_6(g)$, and known enthalpies of formation of -346 kcal mole^{-1} for $WF_5(c)$[1] and of -412 kcal mole^{-1} for $WF_6(g)$[1], an enthalpy of formation of -292 kcal mole^{-1} can be estimated

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* The enthalpy of formation of $WOF_4(s)$ is -359 kcal mole^{-1} (J. BURGESS, I. HAIGH AND R. D. PEACOCK, unpublished determination via alkaline hydrolysis).
** Entropies of tungsten tetrafluoride and of tungsten pentafluoride were estimated by Latimer's method (see The Oxidation States of the Elements and their Potentials in Aqueous Solution, 2nd edn., Prentice-Hall, New Jersey, 1952). The validity of this empirical method of estimating entropies in the present situation is supported by the close agreement between the estimated and experimentally determined values for the entropy of niobium pentafluoride (A. P. BRADY, O. E. MYERS AND J. K. CLAUSS, J. Phys. Chem., 64 (1960) 588). The entropy of tungsten hexafluoride was estimated from vibrational spectroscopy (D. M. ADAMS, I. HAIGH AND R. D. PEACOCK, unpublished work).

for WF_4*. From the enthalpies of formation reported above, one can now estimate the enthalpy changes for reactions (1), (2) and (3) above. All three decompositions have large positive enthalpies, $+41$, $+86$ and $+61$ kcal mole^{-1} respectively, and are thus thermochemically unfavourable.

Re-distribution reactions of the chloride fluorides can most easily be discussed with reference to Figure 1, in which enthalpies of formation of the series of compounds WF_xCl_{6-x} in their standard states are plotted as a function of composition. The proximity of the chloride fluoride points to the straight line joining the $x - 0$ and $x - 6$ extremes, WCl_6 and WF_6 respectively, indicates that re-distribution reactions will be approximately thermoneutral. Entropy–temperature contributions will therefore be significant in determining the sign and magnitude of free energy changes; the production of gaseous WF_6 will obviously favour re-distribution in putative reactions in which it is a product. At temperatures other than 25°, the variation of enthalpies with temperature, and particularly any relevant enthalpies of phase changes, will also be important.
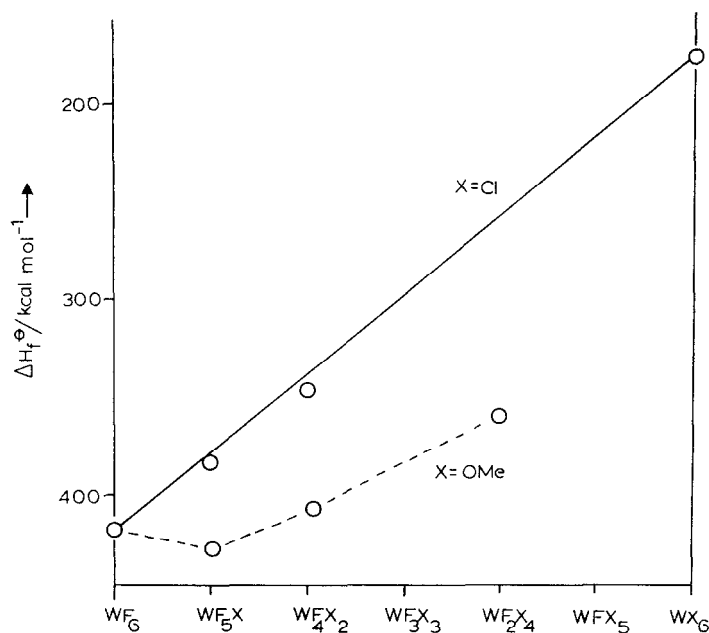

Fig. 1. Enthalpies of formation of tungsten(VI) chloride fluorides and methoxide fluorides as a function of composition.

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* Another estimate for the enthalpy of formation of tungsten tetrafluoride can be similarly derived from the observation[11] that the disproportionation $3WF_4 \rightleftharpoons 2WF_6 + W$ must have an equilibrium constant close to unity at temperatures around 100°; hence $\Delta H_f°(WF_4(s)) \cong -288$ kcal mole^{-1}.

Thus in the chloride fluoride series decompositions are thermochemically unfavourable but re-distribution reactions not unfavourable, whereas in the methoxide fluoride series re-distribution reactions are unfavourable while decompositions are favourable. The differences in re-distribution behaviour are clear from Figure 1. These differences in thermochemical patterns thus mirror the reported differences in chemical behaviour. The source of these thermochemical differences remains a subject for speculation. One feels that whereas tungsten(VI)–fluorine and tungsten(VI)–chlorine bonds are very similar electronically, tungsten(VI)–oxygen bonds differ significantly in that there is an important $p\pi$–$d\pi$ contribution in the last named. Our closely related current investigation of the tungsten(VI) oxide fluoride series of compounds $WO_xF_{(6-2x)}$ is at present hampered by our inability to prepare samples of WO_2F_2.

The above discussion of chemical reactivity in terms of thermochemical results is obviously limited by a lack of knowledge of entropies of compounds. The entropy of WF_5Cl has been estimated from vibrational spectroscopy[12]; we hope eventually to determine entropies of related compounds so that we can offer a more detailed discussion in terms of free energies. We also hope to develop apparatus to determine enthalpies of vaporisation and of sublimation so that we can, from our reported enthalpies of formation, estimate and discuss mean bond energies of molecules of this type.

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