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THE ENTHALPY OF FORMATION OF MOLYBDENUM DIOXODIFLUORIDE

M. J. ATHERTON, J. BURGESS, J. H. HOLLOWAY, and N. MORTON

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

SUMMARY

The enthalpy of hydrolysis of solid molybdenum dioxodifluoride in alkaline aqueous solution is -231 kJ mol^{-1}. Hence its standard enthalpy of formation has been calculated to be -1089 kJ mol^{-1}.

INTRODUCTION

A number of elements, both in the sp-block and in the transition metal (d and f) series form oxofluorides of composition MO_2F_2 and MOF_4 with the element in oxidation state +6. However there are interesting differences between the relative stabilities of oxofluorides of these formulae, depending on the position of the element, M, in the Periodic Table. For elements in the sp-block or in the actinide series, the stability of the dioxodifluoride seems to be greater than that of the oxotetrafluoride. Thus, for example, SeO_2F_2 is a long-established compound, whereas $SeOF_4$ was only characterised recently [1]. $SeOF_4$ readily disproportionates into SeO_2F_2 and SeF_6, and indeed most reactions which should give $SeOF_4$ give a mixture of SeO_2F_2 and SeF_6 [2]. The case of uranium(VI) is very similar, with UO_2F_2 known for a long time, but UOF_4 reported only a few years ago [3]. Only for sulphur do both oxofluorides, SO_2F_2 and SOF_4, appear comparably stable.

The pattern for the d-block elements differs from this. The compound WOF_4 is considerably more readily accessible and more stable than WO_2F_2, though it has been suggested that the latter is an important constituent of the tungsten-oxygen-fluorine system at incandescent lamp temperatures [4]. $ReOF_4$ exists, but there has not yet been a report of the existence of ReO_2F_2 [5]. Molybdenum appears to behave similarly to tungsten, but there are qualitative indications that CrO_2F_2 may be more stable than $CrOF_4$ [6].

It is generally impossible to measure enthalpies of formation of ternary compounds such as oxofluorides via direct combination of the elements. However, it is possible to make determinations via enthalpies of hydrolysis. This has been achieved satisfactorily for WOF_4 and for $MoOF_4$, using hydrolysis in alkaline media to produce tungstate and molybdate, whose enthalpies of formation are well-established [6]. It is also possible to estimate enthalpies of formation by such indirect methods as mass spectroscopy and gas transport measurements. For WOF_4 these indirect methods gave results which are none too consistent with the more direct determination via alkaline hydrolysis (see below).

Enthalpies of formation of WO_2F_2 and of MoO_2F_2 have not yet been obtained by calorimetric methods, though values obtained by mass spectroscopy are available for both compounds and by gas transport for WO_2F_2 (see below). In this present paper we report the enthalpy of alkaline hydrolysis of MoO_2F_2, and thence determine the standard enthalpy of formation of this compound.

EXPERIMENTAL

Samples of molybdenum dioxodifluoride were prepared by two routes, either the high temperature fluorination of molybdenum dioxodichloride using anhydrous hydrogen fluoride [8,9] or the low temperature fluorination of molybdenum dioxodichloride with xenon difluoride [9].

$\underline{MoO_2Cl_2 + HF}$. Molybdenum dioxodichloride, prepared by passing a Cl_2/O_2 mixture over molybdenum powder in a flow system [10], was weighed into a preseasoned nickel screw-top reactor fitted with a copper gasket. A stoicheiometric amount of anhydrous HF was condensed into the reactor which was then heated to ∿280°C for 4 hr. After cooling and removal of volatiles (HCl) purple, glassy MoO_2F_2 was found in the bottom of the reactor.

$\underline{MoO_2Cl_2 + XeF_2}$. MoO_2Cl_2 was weighed into a preseasoned ¼" FEP tube, which was flare-fitted onto a Kel-F valve. Anhydrous HF, which acts as a moderator for the reaction, was condensed into the tube and XeF_2 was added whilst the contents of the reactor were at -196°C. Reaction occurred on warming to ∿0°C. When all the MoO_2Cl_2 had been consumed the volatiles were removed under dynamic vacuum leaving the involatile MoO_2F_2 in the tube.

Samples of MoO_2F_2 were characterised by mass spectrometry, ^{19}F n.m.r. and infrared spectroscopy and elemental analyses [9].

Enthalpies of alkaline hydrolysis of MoO_2F_2 were determined in an LKB 8700 calorimeter, equipped with a Wheatstone bridge circuit incorporating a Kipp-Zonen BD5 recorder. Details of the operation and calibration of this apparatus have been published elsewhere [7].

RESULTS

Enthalpies of hydrolysis were measured for seven bulbs containing MoO_2F_2, the material being taken from three independently prepared samples of this compound. Each hydrolysis was conducted in sodium hydroxide solution of concentration 1.0 mol dm^{-3}. The mean enthalpy of hydrolysis was -231 ± 4 kJ mol^{-1}; the error limits cited represent the 90% confidence limits [11] of this mean. The equation for this alkaline hydrolysis is

$$MoO_2F_2 + 4OH^- = MoO_4^{2-} + 2F^- + 2H_2O.$$

From our measured enthalpy of hydrolysis, and known standard enthalpies of formation in aqueous solution of hydroxide ion (-230.0 kJ mol^{-1} [12]), molybdate ion (-997.0 kJ mol^{-1} [13]), and fluoride ion (-335.4 kJ mol^{-1} [14]), and of liquid water (-285.8 kJ mol^{-1} [12]), we calculate a value of -1089 kJ mol^{-1} for the standard enthalpy of formation of molybdenum dioxodifluoride in the solid state (at 298 K).

DISCUSSION

Our value for the enthalpy of formation of MoO_2F_2 is rather different from that reported from mass spectroscopic observations. These latter gave $\Delta H_f^\ominus$ (MoO_2F_2(g)) = -1121 kJ mol^{-1} [15], which implies that $\Delta H_f^\ominus$ (MoO_2F_2(s)) is about -1200 kJ mol^{-1}. The situation is similar to that for WOF_4, where direct hydrolysis and mass spectroscopic determinations of the standard enthalpy of formation differ by about 150 kJ mol^{-1} [7].

Values for the standard enthalpies of formation of oxide-fluoride compounds of molybdenum, tungsten, and uranium are listed in Table 1.

TABLE 1

Standard enthalpies of formation ($\Delta H_f^{\ominus}$/kJ mol^{-1}) of oxide fluoride compounds of molybdenum(VI), tungsten(VI), and uranium(VI).

	Molybdenum		Tungsten		Uranium
	Solid	Gas	Solid	Gas	Solid
MO_3	-745[13]	(ca -356)[13]	-843[13]	(ca -293)[13]	-1224[17]
MO_2F_2	-1089	(-1121[a])[13]		(-900[a])[15] (-930[b])[16]	-1651[7]
MOF_4[c]	-1380[7]		-1500[7]	(-1322[a])[15]	
MF_6	-1585(liq)[13]	-1558[13]	-1748(liq)[13]	-1722[13]	-2187[17]

[a] Indirect estimates from mass spectroscopy; [b] indirect estimates from gas transport experiments;

[c] see also ref. [18] for $MoOF_4$, WOF_4.

As enthalpies of sublimation of several of these compounds are not known it is not possible to give data relating solely to the gas or solid state. The values in this Table give some idea of the uncertainties and doubts in some of these enthalpies. Nonetheless, a clear trend of increasing enthalpy of formation is apparent, as are the more negative values for tungsten than for analogous molybdenum compounds. In view of the reported

$$MO_3 < MO_2F_2 < MOF_4 < MF_6 \qquad [\Delta H_f^\ominus \text{ trend}]$$

ease of disproportionation of $SeOF_4$, it is of interest to estimate the enthalpy of disproportionation of MoO_2F_2. For decomposition according to the equation

$$2MoO_2F_2(s) \rightarrow MoOF_4(s) + MoO_3(s)$$

the enthalpy change is +27 kJ mol^{-1} (per mole of MoO_2F_2, at 298 K). For decomposition into the binary compounds

$$3MoO_2F_2(s) \rightarrow MoF_6(\ell) + 2MoO_3(s)$$

the enthalpy change is +64 kJ mol^{-1} (per mole of MoO_2F_2, at 298 K). Thus, assuming small entropy changes, the decompositions of MoO_2F_2 set out in the above equations are not thermochemically favourable. However, the Gibbs free energy change for the disproportionation of MoO_2F_2 into $MoOF_4$ and MoO_3 may be close to zero. It is possible that the Gibbs free energy change for the analogous reaction of WO_2F_2 may be negative, which would help to explain our inability to prepare satisfactorily pure samples of this compound. The data in Table 1 show that the disproportionation of UO_2F_2:

$$3UO_2F_2(s) \rightarrow UF_6(s) + 2UO_3(s)$$

TABLE 2

Standard enthalpies of formation ($\Delta H_f^{\ominus}$/kJ mol^{-1}) of dioxodihalides of molybdenum(VI) and tungsten(VI).

	Molybdenum		Tungsten	
	Solid	Gas	Solid	Gas
MO_2F_2	-1089	(-1121)[15]		-900[c] -930[c]
MO_2Cl_2[a]	-727[19]	-638[19]	-833[22] -837[23]	-715[22] -749[23]
MO_2Br_2	-641[19]	-538[19]	-744[24] -752[25]	-591[24]
MO_2I_2		-416[b][21]	-636[26]	-463[26]

[a] See also ref. [20] for MoO_2Cl_2; [b] indirect estimate from gas transport experiments; [c] see Table 1.

has an enthalpy change of +106 kJ mol^{-1} (per mole of UO_2F_2). Hence the Gibbs free energy change for this reaction, as for its molybdenum analogue, is markedly positive and the reaction thermochemically unfavourable.

While the enthalpies of formation of these oxofluorides are of interest in their own right, they may also in future be of use in the estimation of fluoride ion affinities for these oxofluorides. Such estimates require the preparation of salts such as $CsWOF_5$ [27] and the measurement of their enthalpies of alkaline hydrolysis. They also require the calculation of lattice energies of such salts. Unfortunately, such lattice energy calculations provide the main source of uncertainty in the estimation of halide ion affinities of binary halides, for instance in the derivation of the fluoride ion affinity of WF_5 from salts such as KWF_6 [28]. They are at present impossible to carry out satisfactorily for mixed anions of the WOF_5^- type.

Recent descriptions of sulphur analogues such as WSF_4 and WS_2F_2 [29,30] lead us to hope that an extension of calorimetric studies of oxide fluorides may soon be possible to sulphide fluorides for molybdenum and tungsten.

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