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THE ENTHALPY OF FORMATION OF ReF_4O

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SUMMARY

The enthalpy of formation of $ReF_4O(s)$, determined from the enthalpy of alkaline hydrolysis in the presence of hypochlorite ion, is -1179 ± 4 kJ mol^{-1}.

EXPERIMENTAL

Rhenium tetrafluoride oxide was prepared by O'Donnell's method from the reaction of B_2O_3 with an excess of rhenium hexafluoride [1]. The product was resublimed under a high vacuum and its purity checked by i.r. spectroscopy. Samples of between 60 and 110 mg were transferred to ampoules for the calorimetric determinations, which were conducted at 298.2K in an LKB 8700 calorimeter. The apparatus, calibration, and techniques have been described previously [2]. The hydrolysis of the compound went to completion smoothly within a few seconds in aqueous sodium hydroxide solution (1 mol dm^{-3}) in the presence of sodium hypochlorite solution (8% available Cl [eqn. (1)].* Four separate measurements gave values of -548.0, -549.3, -544.8 and -554.7 kJ mol^{-1} respectively, yielding

$$2\ ReF_4O(s) + 10\ OH^-aq + OCl^-aq \rightarrow 2\ ReO_4^-aq + 8F^-aq + Cl^-aq + 5\ H_2O(\ell) \qquad (1)$$

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* ReO_4^- was formed quantitatively in this reaction without significant gas evolution.

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a mean value of -549 ± 4 kJ mol^{-1}. From this value and the following ancillary standard enthalpies; OH^-aq -230.0 [3], ReO_4^-aq -791.6 [4] F^-aq -335.35 [5], OCl^-aq -107.8 [6], $H_2O(\ell)$ -285.4 [3], the enthalpy of formation of solid ReF_4O was calculated to be -1179 ± 4 kJ mol^{-1}. As the enthalpy of sublimation of ReF_4O is 74.6 kJ mol^{-1} [7] the enthalpy of formation of gaseous ReF_4O is estimated to be -1104 ± 4 kJ mol^{-1} (at 298.2K).

DISCUSSION

The enthalpies of formation of a number of binary halides of rhenium have been determined viz the trichloride, tribromide [8], tetrachloride, tetrabromide [9], pentachloride, hexafluoride [10], and heptafluoride [11]. Of the rhenium halide oxides, only the enthalpy of formation of ReF_5O has hitherto been reported [12]. Unfortunately, the enthalpy of formation of ReO_3 is not known so that it is not possible to make an estimate of the stability of ReF_4O towards its disproportionation products ReO_3 and ReF_6. However, it may be estimated from the data given in Table 1 that the contribution of the Re=O bond towards the total bond enthalpy is 728 kJ mol^{-1} (668 kJ mol^{-1} in $ReOF_5$), while for reaction (2) the enthalpy change is only -82 kJ mol^{-1}.

$$ReOF_4(g) + \tfrac{1}{2}F_2(g) \rightarrow ReOF_5(g) \qquad (2)$$

For reaction (3), which involves the conversion of tetrafluoride oxide to

$$ReOF_4(g) + F_2(g) \rightarrow ReF_6(g) + \tfrac{1}{2}O_2(g) \qquad (3)$$

hexafluoride, the enthalpy change is -229 kJ mol^{-1}, a value which lies close to that of $MoOF_4(g)$ to $MoF_6(g)$ (-232 kJ mol^{-1}).

Rhenium tetrafluoride oxide, unlike the Mo and W analogues, is not easy to prepare in a good yield by any of the available methods. Preparation from the hexafluoride and WOF_4 (eqn. (4)) has not been attempted, but the enthalpy (-63 kJ mol^{-1}) of the gaseous reaction (which is probably close to the ΔG value), suggests that this is worth investigating provided that there are not other complications such as the existence of a stable adduct between the two tetrafluoride oxides.

$$ReF_6(g) + WOF_4(g) \rightarrow ReOF_4(g) + WF_6(g) \qquad (4)$$

TABLE 1

Enthalpies of Formation of Gaseous Hexafluorides and Oxide Tetrafluorides (kJ mol^{-1})

MoF_6	-1557 [13]	$MoOF_4$	-1325 [2] [7]
WF_6	-1721 [13]	WOF_4	-1431 [2] [7]
ReF_6	-1333 [10]	$ReOF_4$	-1104

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