The Enthalpy of Formation of Rhenium Pentafluoride Oxide †

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The enthalpy of hydrolysis of solid ReF$_5$O in alkaline aqueous solution at 298.2 K is −717 kJ mol^{-1}. Thence its enthalpy of formation has been calculated to be −1 229 kJ mol^{-1}.

ENTHALPIES of formation have been reported for a variety of binary halides of rhenium, for example the tribromide,[1] trichloride,[1] tetrachloride,[2] pentachloride,[3] and heptafluoride,[4] but not as yet for any halide oxide of rhenium. It is, of course, not possible to determine enthalpies of formation of halide oxides from their constituent elements by direct combustion or bomb calorimetry. In the case of rhenium(VII) halide oxides it is possible to estimate enthalpies of formation by measuring enthalpies of hydrolysis under alkaline conditions. Here the product is the tetraoxorhenate(VII) anion, whose enthalpy of formation is well established.[5]

There are several oxide fluorides of Re^{VII}, whose preparations have recently been reviewed.[6] In this paper we report the enthalpy of hydrolysis of rhenium pentafluoride oxide in aqueous sodium hydroxide solution, and thence estimate its standard enthalpy of formation.

EXPERIMENTAL

Rhenium pentafluoride oxide was prepared by fluorination of rhenium tetrafluoride oxide in a nickel reactor. A 50% excess of fluorine was used; the reactor was heated at 570 K for 3 h. After the reaction the reactor was cooled to 195 K and the excess of fluorine pumped off. The pentafluoride oxide was purified by resublimation (twice) under high vacuum; its purity was assessed from its Raman spectrum.

The measurements of the enthalpy of hydrolysis were conducted at 298.2 K in an LKB 8700 calorimeter. The apparatus, calibration, and techniques used have been described previously.[7]

RESULTS

The hydrolysis of ReF$_5$O went to completion rapidly and smoothly in aqueous hydroxide solution (1 mol dm^{-3}) [equation (1)]. Four hydrolyses, using ReF$_5$O from two independent preparations, gave a mean enthalpy of alkaline hydrolysis of −717 kJ mol^{-1}. The 90% confidence limits [8] of this value are ±4 kJ mol^{-1}.

$$\mathrm{ReF_5O} + 6[\mathrm{OH}]^- \longrightarrow [\mathrm{ReO_4}]^- + 5\mathrm{F}^- + 3\mathrm{H_2O} \quad (1)$$

The enthalpy of formation of ReF$_5$O was calculated from this enthalpy of hydrolysis and the known enthalpies of formation of the other species involved in the hydrolysis reaction. We used the following values of standard enthalpy of formation (kJ mol^{-1}): hydroxide ion, −230.0; [9] tetraoxorhenate(VII) ion, −791.6; [5] fluoride ion, −335.4 (ref. 10) (in all cases in aqueous solution); and −285.8 for liquid water.[9] These values give −1 229 kJ mol^{-1} for the enthalpy of formation ‡ of solid ReF$_5$O. As the enthalpy of sublimation of this compound is 43 kJ mol^{-1},[11] the enthalpy of formation ‡ of gaseous ReF$_5$O is −1 186 kJ mol^{-1} (at 298.2 K).

DISCUSSION

It is interesting to compare the enthalpy of formation of ReF$_5$O with those of the two closely related binary compounds of Re^{VII}, the heptafluoride and the heptaoxide. The enthalpy of formation of ReF$_7$ is −1 471 (solid) or −1 429 kJ mol^{-1} (gas, 298.2 K).[4,§] The enthalpy of formation of Re$_2$O$_7$ is −1 241 (solid) or −1 101 kJ mol^{-1} (gas, 298.2 K).[12] The value for ReF$_5$O is, as expected, intermediate between these values. The enthalpy change for the disproportionation reaction [equation (2)] is thus 1 kJ mol^{-1} (per mol of ReF$_5$O) for the reactant and products in the solid state, 8 kJ mol^{-1} in the gas phase. These are remarkably small positive values, which may just be sufficient for disproportionation not to be spontaneous, at least in the vicinity of room temperature. (The entropy changes will be small for the all-solid or all-gas reactions, and slightly unfavourable for the latter.)

$$7\mathrm{ReF_5O} \longrightarrow 5\mathrm{ReF_7} + \mathrm{Re_2O_7} \quad (2)$$

The enthalpy change for the reaction of ReF$_5$O with fluorine [equation (3)] in the gas phase is −243 kJ mol^{-1}, whence the Gibbs free-energy change can be estimated as −212 kJ mol^{-1}. Thermochemically it follows that

$$\mathrm{ReF_5O} + \mathrm{F_2} \longrightarrow \mathrm{ReF_7} + \tfrac{1}{2}\mathrm{O_2} \quad (3)$$

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† No reprints available.

‡ Consideration of appropriate enthalpies of dilution suggests that these enthalpies of formation are likely to differ by no more than 1—2 kJ mol^{-1} from the respective standard enthalpies of formation (298.2 K).

§ These values have been recalculated from the data on the enthalpy of alkaline hydrolysis in ref. 4 using the $\Delta H_f^\ominus[\mathrm{F^-(aq)}]$ value of ref. 10.

[1] J. P. King and J. W. Cobble, *J. Amer. Chem. Soc.*, 1960, **82**, 2111; N.B.S. Technical Note 270/4, 1969.

[2] J. Burgess, S. J. Cartwright, I. Haigh, R. D. Peacock, P. Taylor, H. D. B. Jenkins, and K. F. Pratt, *J.C.S. Dalton*, submitted for publication.

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

[4] J. Burgess, J. Fawcett, R. D. Peacock, and D. Pickering, *J.C.S. Dalton*, 1976, 1364.

[5] R. H. Busey, K. H. Gayer, R. A. Gilbert, and R. B. Bevan, *J. Phys. Chem.*, 1966, **70**, 2609.

[6] W. A. Sunder and F. A. Stevie, *J. Fluorine Chem.*, 1975, **6**, 449.

[7] See, for example, J. Burgess, I. Haigh, and R. D. Peacock, *J.C.S. Dalton*, 1974, 1062.

[8] See, for example, E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971, pp. 7—9.

[9] *J. Chem. Thermodynamics*, 1975, **7**, 1; 1976, **8**, 603.

[10] G. K. Johnson, P. N. Smith, and W. N. Hubbard, *J. Chem. Thermodynamics*, 1973, **5**, 793

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

[12] W. T. Smith, L. E. Line, and W. A. Bell, *J. Amer. Chem. Soc.*, 1952, **74**, 4965; G. E. Boyd, J. W. Cobble, and W. T. Smith, *ibid.*, 1953, **75**, 5783.

the preparation of ReF_7 from ReF_5O is more favourable than that from ReF_6, for which the Gibbs free-energy change is *ca.* −36 kJ mol^{-1}.[4] However, only the latter approach seems to have been tried as a preparative method to date. Similarly the Gibbs free-energy change for reaction (4), in the gas phase, can be estimated to be −182 kJ mol^{-1}. Here the apparent thermochemical advantage in preparing ReF_6 may well be outweighed by the likely disadvantage of the presence

$$ReF_5O + \tfrac{1}{2}F_2 \longrightarrow ReF_6 + \tfrac{1}{2}O_2 \qquad (4)$$

of considerable amounts of unchanged ReF_5O and ReF_7 in the ReF_6 produced.

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