

## The Enthalpy of Formation of Rhenium Pentafluoride Oxide †

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

ENTHALPIES of formation have been reported for a variety of binary halides of rhenium, for example the tribromide,<sup>1</sup> trichloride,<sup>1</sup> tetrachloride,<sup>2</sup> pentachloride,<sup>3</sup> and heptafluoride,<sup>4</sup> 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.<sup>5</sup>

There are several oxide fluorides of  $\text{Re}^{\text{VII}}$ , whose preparations have recently been reviewed.<sup>6</sup> 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.<sup>7</sup>

### RESULTS

The hydrolysis of  $\text{ReF}_5\text{O}$  went to completion rapidly and smoothly in aqueous hydroxide solution ( $1 \text{ mol dm}^{-3}$ ) [equation (1)]. Four hydrolyses, using  $\text{ReF}_5\text{O}$  from two



independent preparations, gave a mean enthalpy of alkaline hydrolysis of  $-717 \text{ kJ mol}^{-1}$ . The 90% confidence limits<sup>8</sup> of this value are  $\pm 4 \text{ kJ mol}^{-1}$ .

† No reprints available.

‡ Consideration of appropriate enthalpies of dilution suggests that these enthalpies of formation are likely to differ by no more than  $1-2 \text{ kJ mol}^{-1}$  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  $\Delta H_f^\ominus[\text{F}^-(\text{aq})]$  value of ref. 10.

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

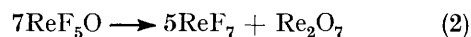
<sup>2</sup> J. Burgess, S. J. Cartwright, I. Haigh, R. D. Peacock, P. Taylor, H. D. B. Jenkins, and K. F. Pratt, *J.C.S. Dalton*, submitted for publication.

<sup>3</sup> J. Burgess, C. J. W. Fraser, I. Haigh, and R. D. Peacock, *J.C.S. Dalton*, 1973, 501.

The enthalpy of formation of  $\text{ReF}_5\text{O}$  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 ( $\text{kJ mol}^{-1}$ ): hydroxide ion,  $-230.0$ ; <sup>9</sup> tetraoxorhenate(VII) ion,  $-791.6$ ; <sup>5</sup> fluoride ion,  $-335.4$  (ref. 10) (in all cases in aqueous solution); and  $-285.8$  for liquid water.<sup>9</sup> These values give  $-1\,229 \text{ kJ mol}^{-1}$  for the enthalpy of formation ‡ of solid  $\text{ReF}_5\text{O}$ . As the enthalpy of sublimation of this compound is  $43 \text{ kJ mol}^{-1}$ ,<sup>11</sup> the enthalpy of formation † of gaseous  $\text{ReF}_5\text{O}$  is  $-1\,186 \text{ kJ mol}^{-1}$  (at 298.2 K).

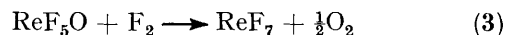
### DISCUSSION

It is interesting to compare the enthalpy of formation of  $\text{ReF}_5\text{O}$  with those of the two closely related binary compounds of  $\text{Re}^{\text{VII}}$ , the heptafluoride and the hepta-oxide. The enthalpy of formation of  $\text{ReF}_7$  is  $-1\,471$  (solid) or  $-1\,429 \text{ kJ mol}^{-1}$  (gas, 298.2 K).<sup>4,§</sup> The enthalpy of formation of  $\text{Re}_2\text{O}_7$  is  $-1\,241$  (solid) or  $-1\,101 \text{ kJ mol}^{-1}$  (gas, 298.2 K).<sup>12</sup> The value for  $\text{ReF}_5\text{O}$  is, as expected, intermediate between these values. The enthalpy change for the disproportionation reaction [equation (2)] is thus  $1 \text{ kJ mol}^{-1}$  (per mol of  $\text{ReF}_5\text{O}$ ) for the reactant and products in the solid state,  $8 \text{ kJ mol}^{-1}$  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.)

The enthalpy change for the reaction of  $\text{ReF}_5\text{O}$  with fluorine [equation (3)] in the gas phase is  $-243 \text{ kJ mol}^{-1}$ ,



whence the Gibbs free-energy change can be estimated as  $-212 \text{ kJ mol}^{-1}$ . Thermochemically it follows that

<sup>4</sup> J. Burgess, J. Fawcett, R. D. Peacock, and D. Pickering, *J.C.S. Dalton*, 1976, 1364.

<sup>5</sup> R. H. Busey, K. H. Gayer, R. A. Gilbert, and R. B. Bevan, *J. Phys. Chem.*, 1966, **70**, 2609.

<sup>6</sup> W. A. Sunder and F. A. Stevie, *J. Fluorine Chem.*, 1975, **6**, 449.

<sup>7</sup> See, for example, J. Burgess, I. Haigh, and R. D. Peacock, *J.C.S. Dalton*, 1974, 1062.

<sup>8</sup> See, for example, E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971, pp. 7-9.

<sup>9</sup> *J. Chem. Thermodynamics*, 1975, **7**, 1; 1976, **8**, 603.

<sup>10</sup> G. K. Johnson, P. N. Smith, and W. N. Hubbard, *J. Chem. Thermodynamics*, 1973, **5**, 793.

<sup>11</sup> G. H. Cady and G. B. Hargreaves, *J. Chem. Soc.*, 1961, 1568.

<sup>12</sup> 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  $\text{ReF}_7$  from  $\text{ReF}_5\text{O}$  is more favourable than that from  $\text{ReF}_6$ , for which the Gibbs free-energy change is *ca.*  $-36 \text{ kJ mol}^{-1}$ .<sup>4</sup> 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  $-182 \text{ kJ mol}^{-1}$ . Here the apparent thermo-

chemical advantage in preparing  $\text{ReF}_6$  may well be outweighed by the likely disadvantage of the presence



of considerable amounts of unchanged  $\text{ReF}_5\text{O}$  and  $\text{ReF}_7$  in the  $\text{ReF}_6$  produced.

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