The Exchange Reaction between Rhenium Hexafluoride and Boron Trichloride and Enthalpies of Formation of Rhenium Pentachloride and Rhenium Hexafluoride

By **J. Burgess, (Mrs.) C. J. W. Fraser, I. Haigh,** and **R. D. Peacock,*** Department of Chemistry, The University, Leicester LE1 7RH

Enthalpies of formation of $ReCl_5$, $-86{\cdot}1 \pm 0{\cdot}8$ kcal mol^{-1}, and ReF_6, $-322{\cdot}6 \pm 2{\cdot}3$ kcal mol^{-1}, have been estimated from hydrolysis measurements. The reaction of rhenium hexafluoride with boron trichloride, under various conditions, has been shown to yield rhenium pentachloride as the only major solid phase; the previously reported hexachloride has not been detected.

FEW data are available on the thermochemical properties of rhenium–halogen compounds, although such information is useful in relation to discussions of stabilities. An early estimate of the heat of formation of rhenium hexafluoride was made from direct measurement of the heat evolved on reaction of the constituent elements;[1] precise data are available for potassium hexachlororhenate(IV), K_2ReCl_6,[2] rhenium trichloride[3] and tribromide.[4] The heat of formation of rhenium pentachloride has been estimated[5] from that of the trichloride, and thermochemical data[6] established for the equilibrium $ReCl_5(c) \rightleftharpoons ReCl_3(c) + Cl_2(g)$.

We report measurements of the enthalpy of hydrolysis of rhenium hexafluoride, ReF_6, and of rhenium pentachloride, $ReCl_5$, from which the heats of formation of these compounds have been estimated. We have also investigated the exchange reaction between rhenium hexafluoride and boron trichloride in an attempt to isolate $ReCl_6$, which is purported to be formed from direct reaction of the constituent elements.[4] Whilst the present work was in progress, further studies were published[7,8] in which the formation of $ReCl_6$ was partially disproved; however its preparation in good yield from the exchange reaction between ReF_6 and various non-metallic chlorides, including BCl_3, has been reported.[7]

EXPERIMENTAL

Preparations.—Rhenium pentachloride was prepared from the reaction of rhenium sponge (Johnson, Matthey) with dry chlorine at 400 °C in a flow system. The metal was reduced with hydrogen at 500 °C before use to minimise

---

[1] O. Ruff and W. Kwasnik, *Z. anorg. Chem.*, 1934, **220**, 96.

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

[3] J. P. King and J. W. Cobble, *J. Amer. Chem. Soc.*, 1960, **82**, 2111.

[4] R. Colton, *Nature*, 1962, **194**, 374; D. Brown and R. Colton, *J. Chem. Soc.*, 1964, 714.

[5] Nat. Bur. Stand., Technical Note 270/4, 1969, and R. H. Schumm, personal communication.

[6] N. V. Baryshnikov and A. N. Zelikman, *Izvestiya Vysshikh Uchebnykh Zavedenii, Tsvetnaya Metallurgiya*, 1962, **5**, 98.

[7] J. H. Canterford, T. A. O'Donnell, and A. B. Waugh, *Austral. J. Chem.*, 1971, **24**, 243; J. H. Canterford and A. B. Waugh, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 395.

[8] A. Guest and C. J. L. Lock, *Canad. J. Chem.*, 1971, **49**, 603.

formation of oxide chloride compounds. The crude product was redistilled in chlorine and remaining traces of volatile oxide chloride compounds were removed *in vacuo*. *X*-Ray powder photography indicated that the pentachloride possessed a unit cell identical with that previously reported,[9] and the i.r. spectrum demonstrated the absence of absorption peaks in the 1000 cm^{-1} region (Found: Re, 51·0. Calc. for $ReCl_5$: Re, 51·2%).

Rhenium hexafluoride was prepared from its constituent elements by a flow method. The product [10] was purified by fractional distillation and by passing over rhenium sponge at about 500 °C, which converts ReF_7 to ReF_6 and volatile $ReOF_5$ to slightly volatile $ReOF_4$. The purified compound was stored at −30 °C over sodium fluoride in Pyrex bulbs (Found: F, 37·7; Re, 61·8. Calc. for ReF_6: F, 38·0; Re, 62·0%).

Boron trichloride (B.D.H. Laboratory grade) was purified by vacuum distillation and stored over phosphorus pentoxide. Hydrogen chloride and chlorine were dried by passing through a solution of sulphuric acid and over a 30 × 2·5 cm column of phosphorus pentoxide, followed by vacuum fractionation.

Reaction of ReF_6 *with* BCl_3.—(*a*) *With an excess of* BCl_3 *and* Cl_2. Rhenium hexafluoride (*ca.* 2 g), boron trichloride (*ca.* two-fold excess over ReF_6), and chlorine were successively sublimed or distilled *in vacuo* into a vessel maintained at −196 °C. The temperature was allowed to rise to −50 °C. Initially the solution turned pale green, and deepened through dark green to dark brown; after about 1 h a dark brown crystalline solid began to precipitate. After 6 h the temperature was allowed to rise slowly to 0 °C and the volatile products collected in a trap at −196 °C; the remaining brownish-black crystalline solid was freed from volatile materials *in vacuo* (12 h). Debye *X*-ray powder patterns indicated the crystalline product to be $ReCl_5$, and i.r. spectroscopic measurements demonstrated the absence of Re–O frequencies. Volatile products were distilled *in vacuo* into successive traps held at −30, −78, and −180 °C. The fraction at −180 °C was found to consist of BF_3, $BClF_2$, and BCl_2F which were identified by ^{19}F n.m.r. spectroscopy. The fraction at −78 °C consisted of a bright yellow crystalline solid, with all the physical characteristics of ReF_6, and a small quantity of a bright green crystalline solid (too little to permit characterisation). The trap at −30 °C contained dark red and brown solids, the quantities of which were always too small to permit further separation and characterisation.

(*b*) *With an excess of* BCl_3 *in the presence of* HCl. The reaction took a similar course to that described in (*a*), but the dark brownish-green crystalline solid appeared in a shorter time. After 3 h, the volatile products were collected as in (*a*), and the solid, after similar treatment, was shown to give an *X*-ray powder photograph identical with that of $ReCl_5$. In the volatile products it was again possible to identify BF_3, $BClF_2$, and BCl_2F; further quantities of the greenish-brown solid were obtained if the temperature was maintained at −30 °C for a further period.

(*c*) *With an excess of* BCl_3. Reaction mixtures were maintained at −30 and 0 °C respectively; both behaved in the same way, turning initially light green, then dark green, after which a dark greenish-brown crystalline solid precipitated. The compounds BF_3, $BClF_2$, BCl_2F, and ReF_6 were again identified among the volatile products, and, as in (*b*), further quantities of the dark greenish-brown crystals were obtained by maintaining the volatile products either at −30 or 0 °C for 24 h. The solids again gave Debye *X*-ray powder patterns identical with that of $ReCl_5$.

Spectroscopic Measurements.—^{19}F N.m.r. measurements were made on a Varian model DA60 spectrometer. I.r. spectra were recorded using a Perkin-Elmer 225 instrument.

Thermochemical Measurements.—The calorimeter consisted of a Dewar vessel of about 150 ml capacity, equipped with a thermistor, stirrer, and heater for calibration purposes and closed with a Teflon stopper attached to an isothermal copper shield. It was suspended in a water bath maintained at 25·0 °C by a standard contact thermometer, relay, and heater arrangement. The compound to be (oxidatively) hydrolysed was contained in a thin-walled glass bulb of known volume between 5 and 15 ml. The bulb was fused to the glass stirrer and could be broken against a polytetrafluoroethylene-coated metal spike within the calorimeter. Heat changes in the calorimeter, arising from chemical reaction or heater calibration, were detected by a thermistor incorporated in a Wheatstone bridge network. Changes in the resistance of the thermistor were monitored by a Kipp BD-2 or Kipp–Zonen BD-5 recorder incorporated in the bridge network.

The reliability of this apparatus was checked by determinations of the heats of (i) precipitation of silver chloride from aqueous solution, (ii) hydrolysis of tungsten hexafluoride in aqueous sodium hydroxide solution, and (iii) solution of tris(hydroxymethyl)aminomethane (Tris) in 0·1M-hydrochloric acid. Six determinations of (i) gave a value of −15·7 (s.d. 0·2); lit.[11] −15·70 kcal mol^{-1}.[*] Six determinations of (ii) gave a value for $\Delta H_f^\circ(WF_6,g)$ of −411·8 (s.d. 1·4); lit.[12] −411·5 kcal mol^{-1}. The measured heat of solution of Tris in 0·1M-hydrochloric acid was −6·99; lit.[13] −7·11 kcal mol^{-1}.

RESULTS

Rhenium pentachloride hydrolysed rapidly in oxygen-free dilute sodium hydroxide solution at 25 °C to produce rhenium dioxide and tetraoxorhenate(VII) ions [equation (1)]. The reaction was complete within 2 min. The heat

$$3ReCl_5 + 16OH^- \xrightarrow{3\Delta H_1} 2[ReO_2,2H_2O] + ReO_4^- + 15Cl^- + 4H_2O \quad (1)$$

of hydrolysis in 0·106M-NaOH was, within experimental uncertainty, the same as that in 1·004M-NaOH. We therefore averaged the ten values at both sodium hydroxide concentrations to give a mean value for ΔH_1 of 137·0 kcal mol^{-1} (standard error of the mean 0·2 kcal mol^{-1}). The enthalpy of formation of solid rhenium pentachloride at 25 °C was thence estimated as $\Delta H_f^\circ[ReCl_5(c)] = -85{\cdot}0 \pm 2{\cdot}0$ kcal mol^{-1},[†] using the following enthalpies of formation (kcal mol^{-1}): −241·8, $ReO_2,2H_2O(c)$;[2] −189·2, ReO_4^--

---

[*] 1 kcal = 4·18 kJ.

[†] The estimated error includes the uncertainty quoted for the reported value of $\Delta H_f^\circ[ReO_2,2H_2O(c)]$.

[9] K. Mucker, G. S. Smith, and Q. Johnson, *Acta Cryst.*, 1968, **B 24**, 874.

[10] J. C. Malm and H. Selig, *J. Inorg. Nuclear Chem.*, 1961, **20**, 189.

[11] G. J. Ewing and C. J. Mazac, *Analyt. Chem.*, 1966, **38**, 1575.

[12] O. E. Myers and A. P. Brady, *J. Phys. Chem.*, 1960, **64**, 591; P. A. G. O'Hare and W. N. Hubbard, *ibid.*, 1966, **70**, 3353.

[13] J. O. Hill, G. Ojelund, and I. Wadso, *J. Chem. Thermodynamics*, 1969, **1**, 111.

(aq);[14] −39·952, $Cl^-(aq)$;[15] −54·97, $OH^-(aq)$;[15] and −68·315, $H_2O(l)$.[15]

In the presence of a sufficient excess of hypochlorite ions, rhenium pentachloride was rapidly oxidised in alkaline solution to tetraoxorhenate(VII) ions (*cf.* K_2ReCl_6)[2] [equation (2)]. Nine determinations of ΔH_2 gave a mean

$$ReCl_5 + ClO^- + 6OH^- \xrightarrow{\Delta H_2} ReO_4^- + 6Cl^- + 3H_2O \quad (2)$$

value of −191·7 kcal mol⁻¹ (standard error of the mean 0·3 kcal mol⁻¹). From this value, the heat of formation of $ClO^-(aq)$ (−26·2 kcal mol⁻¹),[16] and the relevant heats of formation quoted in the previous paragraph, the estimated enthalpy of formation of solid rhenium pentachloride at 25 °C was $\Delta H_f^{\ominus}[ReCl_5(c)] = -86{\cdot}1 \pm 0{\cdot}8$ kcal mol⁻¹, in good agreement with the value derived by the alternative route described in the previous paragraph.

Rhenium hexafluoride vapour hydrolysed rapidly in the presence of alkaline hypochlorite ions to give tetraoxorhenate(VII) and fluoride ions [equation (3)]. Ten

$$ReF_6 + ClO^- + 14OH^- \xrightarrow{\Delta H_3} 2ReO_4^- + 12F^- + Cl^- + 7H_2O \quad (3)$$

determinations of ΔH_3 gave a mean value of −204·8 kcal mol⁻¹ (standard error of the mean 1·0 kcal mol⁻¹). From this mean value, the heat of formation of $F^-(aq)$ (−79·50 kcal mol⁻¹),[15] and the relevant heats of formation quoted in the preceding two paragraphs, the enthalpy of formation of gaseous rhenium hexafluoride was estimated to be $\Delta H_f^{\ominus}[ReF_6(g)] = -322{\cdot}6 \pm 2{\cdot}3$ kcal mol⁻¹.*

DISCUSSION

The agreement between our two values for the heat of formation of $ReCl_5$ is remarkably good, especially if the uncertainty in the heat of formation of $ReO_2,2H_2O(c)$ is taken into account. Busey *et al.*[2] noted a marked difference between values of $\Delta H_f^{\ominus}[K_2ReCl_6(c)]$ estimated from the hydrolysis reaction on the one hand and the hypochlorite-ion oxidation on the other, which they attributed to 'ageing' of $ReO_2,2H_2O(c)$. That no analogous difference appears in the present work is probably connected with the rapid hydrolysis of $ReCl_5$ in alkali (perhaps with local heating and thereby rapid 'ageing' of the rhenium dioxide precipitate) compared with the slower rate of hydrolysis (linked with the rate of solution of the crystals) of potassium hexachlororhenate(IV) in alkaline solution. Our results are also in good agreement, within the limits of experimental uncertainty, with that (89·1 ± 3·7 kcal mol⁻¹) derived from the enthalpy of formation of rhenium trichloride *via* the thermodynamic parameters determined for the equilibrium $ReCl_3 + Cl_2 \rightleftharpoons ReCl_5$.[5,6] We therefore propose values of −88·1 ± 0·8 kcal mol⁻¹ for $\Delta H_f^{\ominus}[ReCl_5(c)]$ and −322·6 ± 2·3 kcal mol⁻¹ for $\Delta H_f^{\ominus}[ReF_6(g)]$.

From the above results, and using heats of formation of $BCl_3(g)$ and $BF_3(g)$ of −96·5 and −271·75 kcal mol⁻¹ respectively, the enthalpy for the overall exchange reaction (4) may be estimated to be $\Delta H_4 = -115$

$$ReF_6(g) + 2BCl_3(g) \xrightarrow{\Delta H_4} ReCl_5(c) + Cl_2(g) + 2BF_3(g) \quad (4)$$

kcal mol⁻¹. The free-energy change [using values of S^0 (cal K⁻¹ mol⁻¹): 69·31, $BCl_3(g)$; 60·71, $BF_3(g)$; 82, $ReF_6(g)$;[17] and 55 (est.), $ReCl_5(c)$] may be estimated[18] to be *ca.* 117 kcal mol⁻¹. This reaction should therefore, from a purely thermodynamic point of view, go to completion at 25 °C. The experimental data indicate, however, that the rate of reaction is not rapid even at 25 °C in the presence of an excess of boron trichloride, and appears to be slower if the temperature is lowered or if the reactants are diluted with dry liquid chlorine or liquid hydrogen chloride. These results are not dissimilar from those already obtained for the equivalent exchange reactions involving tungsten hexafluoride[19] but, unlike the latter case, there is little evidence of the formation of intermediate chloride fluoride compounds, even in the presence of HCl (contrast WF_6[19]), and, in particular, $ReClF_5$[20] does not appear in readily identifiable amounts.

The final product from the exchange reactions was identified in each experiment as the pentachloride, $ReCl_5$, and the specimens in every case were sufficiently crystalline to indicate a strong possibility that they had been formed directly from solution rather than by the dry decomposition of another solid phase such as a hexachloride. This result is not in agreement with that of Canterford *et al.*,[7] who claim that $ReCl_6$ is formed in good yield from this and similar exchange reactions as a lower melting, appreciably volatile, solid (m.p. *ca.* 30 °C).[4] Since these authors used techniques rather different from those described above, the present work does not disprove their conclusion, but it should be pointed out that the properties of the material as reported by them are not those expected for $ReCl_6$; it is more probable that $ReCl_6$ forms a solid similar in structure[21] and physical properties to WCl_6[21,22] and hence has a similar melting point (260—300 °C).

Extrapolation of existing thermochemical data, including the present values of $\Delta H_f^{\ominus}$ for $ReCl_5$ and ReF_6, is not very helpful in this connection, since the predicted $\Delta H_f^{\ominus}$ for $ReCl_6$ could lie between −85 and −100 kcal mol⁻¹; these figures would give ΔG^0 values

---

* The estimated error represents the 95% confidence limits of the quoted value, based on the standard error of the mean of ΔH_3.

[14] G. E. Boyd, J. W. Cobble, and W. T. Smith, *J. Amer. Chem. Soc.*, 1953, **75**, 5.

[15] Nat. Bur. Stand., Technical Note 270/2, 1966.

[16] J. E. McDonald, J. P. King, and J. W. Cobble, *J. Phys. Chem.*, 1960, **64**, 1345.

[17] D. M. Adams, I. Haigh, and R. D. Peacock, unpublished calculations based on vibrational spectra.

[18] W. M. Latimer, 'Oxidation Potentials,' 2nd edn., Prentice-Hall, New Jersey, 1952, p. 311.

[19] G. W. Fraser, C. J. W. Gibbs, and R. D. Peacock, *J. Chem. Soc. (A)*, 1970, 1708.

[20] R. D. Peacock and D. F. Stewart, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 255.

[21] J. A. A. Ketelaar, C. W. van Oosterhaut, and P. B. Braun, *Rec. Trav. chim.*, 1943, **62**, 597; D. K. Smith, R. L. Landingham, G. S. Smith, and Q. Johnson, *Acta Cryst.*, 1968, **B24**, 1563.

[22] J. E. Fergusson in 'Halogen Chemistry,' vol. 3, ed. V. Gutmann, Academic Press, London, 1967.

for the reaction $ReCl_6(c) \longrightarrow ReCl_5(c) + \frac{1}{2}Cl_2(g)$ of -9 and $+6$ kcal mol^{-1} respectively. It should also be noted that, although tungsten hexachloride is formed fairly rapidly from the exchange reaction between WF_6 and BCl_3,[19] there is some evidence [22] to suggest that solutions of WCl_6 in inert solvents such as CCl_4 slowly decompose to the pentachloride and chlorine; indeed, it was to minimise this possibility that chlorine was added to some of our ReF_6–BCl_3 reaction mixtures. Although Canterford *et al.* were able to show from i.r. measurements that their material did not contain $ReOCl_4$ (which has very similar physical properties), the observed volatility points to the presence of combined oxygen or fluorine; the former, in particular, is very difficult to eliminate from rhenium–halogen systems. We conclude that the positive evidence for $ReCl_6$ is not yet sufficiently clear to substantiate claims for the existence of this compound.

We are grateful to the University of Leicester for a research scholarship (to C. J. W. F.), to the S.R.C. for a research studentship (to I. H.) and for generous support, and to the National Bureau of Standards for details of the calculations leading to the value for $\Delta H_f^{\ominus}[ReCl_5(c)]$.[5]

[2/1914 *Received*, 14*th August*, 1972]