THE ENTHALPY OF FORMATION OF $ReF_5(NCl)$

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SUMMARY

The compounds $ReF_5(NCl)$ and $ReF_5(NF)$, which contain Re in the +7 state, have recently been isolated and their crystal structures determined [1]. In this note we report on the calorimetry of alkaline hydrolysis of $ReF_5(NCl)$, from which a value of the enthalpy of formation of the compound may be calculated.

EXPERIMENTAL

The compound $ReF_5(NCl)$ was prepared as described previously [1]. Samples of between 10 and 20 mg were transferred to ampoules for the calorimetric determinations, which were carried out as described elsewhere, using an LKB 8700 instrument [2]. The hydrolysis was conducted in 1.0 mol dm^{-3} KOH (2 determinations) and 0.1 mol dm^{-3} KOH (1 determination), using about 25 ml of the appropriate solution for each determination. The apparatus was calibrated against the enthalpy of solution of potassium chloride [3]. Values for $\Delta H_{hydr.}$ of -425, -422, and -419 kJ mol^{-1} were obtained, giving an average of -422 $\pm$ 3 kJ mol^{-1}.

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In alkaline solution the hydrolysis of $ReF_5(NCl)$ is believed to proceed primarily according to the equation:

$$ReF_5(NCl)_{(s)} + 7OH^-_{aq} \rightarrow ReO^-_{4\ aq} + 5F^-_{aq} + NH_{3\ aq} + OCl^-_{aq} + 2H_2O(\ell)$$

From the above enthalpy of hydrolysis, and from the following ancillary standard enthalpies; OH^-_{aq} -230 [4], $ReO^-_{4\ aq}$ - 791.6 [5], F^-_{aq} -335.35 [6], $NH_{3\ aq}$ -80.3 [4], OCl^-_{aq} -107.8 [7], $H_2O(\ell)$ -285.8 [4], the enthalpy of formation of $ReF_5(NCl)_{(s)}$ is calculated to be -1195 kJ mol^{-1}.

Some idea of the rhenium nitrogen bond strength in $ReF_5(NCl)$, which is formally a double bond, may be obtained by assuming a reasonable value for $\Delta H_{sub}\ (ReF_5(NCl))_{(s)}$ (70 kJ mol^{-1}), and taking the Re-F bond strength to be the same as in ReF_7 (393 kJ mol^{-1} (calc. from [8]) and the N-Cl contribution to be the same as in NCl_3 (193 kJ mol^{-1}) [9]. The enthalpy of atomisation of $ReF_5(NCl)_{(g)}$ is hence calculated to be 2884 kJ mol^{-1}, and the Re=N bond strength to be about 725 kJ mol^{-1}. However, the crystal structure of $ReF_5(NCl)$ [1] shows the N-Cl distance to be only 1.56 Å compared to 1.75 A in $HNCl_2$ 10 , so it is likely that the real N-Cl bond strength is significantly greater than 193 kJ mol^{-1} and consequently the 725 kJ mol^{-1} figure for Re=N must be regarded as a maximum value. Nevertheless, it is clearly comparable with Re=O in $ReOF_5$ (620 kJ mol^{-1}) [11] and is considerably stronger than W-N in WF_5N_3 ($\sim$ 320 kJ mol^{-1}) [12].

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