

THE ENTHALPY OF FORMATION OF $\text{ReF}_5(\text{NCl})$

J. BURGESS, J. FAWCETT and R. D. PEACOCK

Department of Chemistry, University of Leicester, Leicester LE1 7RH (U.K.)

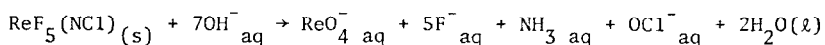
SUMMARY

The compounds $\text{ReF}_5(\text{NCl})$ and $\text{ReF}_5(\text{NF})$, 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 $\text{ReF}_5(\text{NCl})$, from which a value of the enthalpy of formation of the compound may be calculated.

EXPERIMENTAL

The compound $\text{ReF}_5(\text{NCl})$ 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 ΔH_{hydr} of -425, -422, and -419 kJ mol^{-1} were obtained, giving an average of $-422 \pm 3 \text{ kJ mol}^{-1}$.

In alkaline solution the hydrolysis of $\text{ReF}_5(\text{NCl})$ is believed to proceed primarily according to the equation:



From the above enthalpy of hydrolysis, and from the following ancillary standard enthalpies; OH^-_{aq} -230 [4], $\text{ReO}_4^-_{\text{aq}}$ - 791.6 [5], F^-_{aq} -335.35 [6], NH_3_{aq} -80.3 [4], OCl^-_{aq} -107.8 [7], $\text{H}_2\text{O}(\ell)$ -285.8 [4], the enthalpy of formation of $\text{ReF}_5(\text{NCl})_{(s)}$ is calculated to be $-1195 \text{ kJ mol}^{-1}$.

Some idea of the rhenium nitrogen bond strength in $\text{ReF}_5(\text{NCl})$, which is formally a double bond, may be obtained by assuming a reasonable value for $\Delta H_{\text{sub}}(\text{ReF}_5(\text{NCl}))_{(s)}$ (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 $\text{ReF}_5(\text{NCl})_{(g)}$ 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 $\text{ReF}_5(\text{NCl})$ [1] shows the N-Cl distance to be only 1.56 \AA compared to 1.75 \AA 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 ($\sim 320 \text{ kJ mol}^{-1}$) [12].

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