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THE ENTHALPY OF FORMATION OF TUNGSTEN AZIDE PENTAFLUORIDE

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SUMMARY

The enthalpy of hydrolysis of solid tungsten azide pentafluoride in alkaline aqueous solution (1.0 mol dm^{-3} KOH; 298.2K) is -578 kJ mol^{-1}. Hence its enthalpy of formation is -1170 kJ mol^{-1}.

INTRODUCTION

The preparation and properties of tungsten azide pentafluoride, WF_5N_3, have recently been published [1]. We now report its enthalpy of solution in alkaline aqueous medium. Hence we derive a value for its enthalpy of formation, and discuss the thermodynamic implications of this value.

EXPERIMENTAL

The compound WF_5N_3 was prepared as described previously [1]. Samples of between 25 and 50 mg were transferred to ampoules for the calorimetric determinations. These were carried out in the manner, and using the apparatus, based on an LKB 8700 calorimeter vessel, described elsewhere [2]. The hydrolyses were conducted in 1.0 mol dm^{-3} KOH, using about 120 cm^3 of this solution for each determination. The apparatus was calibrated against the enthalpy of solution of potassium chloride [3].

RESULTS

Three samples of WF_5N_3 were successfully hydrolysed. Seven other samples exploded in the ampoules before they could be hydrolysed. The measured enthalpies of hydrolysis (298.2K) were -580, -577, and -578 kJ mol^{-1}. The uncertainties attendant on calibration are $\pm$ 4 kJ mol^{-1} for each determination; the likely uncertainties in the enthalpies of hydrolysis arising from other causes will be rather larger than this.

DISCUSSION

From the measured enthalpy of hydrolysis, -578 kJ mol^{-1}, and the auxiliary data in Table 1, the enthalpy of formation of $WF_5N_3(s)$ is calculated from the equation

$$WF_5N_3(s) + 8OH^-aq \longrightarrow WO_4^{2-}aq + 5F^-aq + N_3^-aq + 4H_2O(\ell).$$

TABLE 1

Enthalpies of formation of auxiliary species (kJ mol^{-1})

OH^-aq	-230 [4]	$N_{3(g)}$	439 [7]
$H_2O(\ell)$	-285.8 [4]	$WF_{6(g)}$	-1723 [8]
F^-aq	-335.35 [5]	$W_{(g)}$	837 [9]
$WO_4^{2-}aq$	-1073.2 [6]	$F_{(g)}$	79.39 [5]
N_3^-aq	260.1 [4]		

To make an estimate of the strength of the W-N band in WF_5N_3 a value of ΔH_{sol} (WF_5N_3) is required; for the present we assume this to be 35 kJ mol^{-1}. This gives $\Delta H_f(WF_5N_{3(g)})$ = -1180 kJ mol^{-1}, and the enthalpy of the change $WF_5N_{3(g)} \rightarrow W_{(g)} + 5F_{(g)} + N_{3(g)}$ is thence estimated to be 2853 kJ mol^{-1}. The enthalpy of the process $WF_{6(g)} \rightarrow W_{(g)} + 6F_{(g)}$ is 3036 kJ mol^{-1}, giving D (W-F) = 506 kJ mol^{-1} and hence D (W-N) $\sim$ 323 kJ mol^{-1}. This figure depends on the assumption that the average W-F

bond strength in WF_5N_3 is the same as in WF_6, and we note that the average W-F bond distance in WF_5N_3 is 1.84Å [1], near to that in WF_6 vapour (1.826Å)[10]. It is interesting to compare D(W-N) with D(W-Cl) in WF_5Cl and WF_4Cl_2 [2]; similar calculations give D(W-Cl) = 397 kJ mol^{-1} respectively in WF_5Cl and 389 kJ mol^{-1} in WF_4Cl_2.

Tungsten azide pentafluoride is an unstable compound, and the thermochemical properties reflect this. For example, the enthalpy of the reaction

$$6WF_5N_{3(s)} \rightarrow W_{(s)} + 5WF_{6(g)} + 9N_{2(g)}$$

which would be strongly favoured by entropy, is calculated to be -1325 kJ mol^{-1}, i.e. about -220 kJ mol^{-1} per mol of WF_5N_3.

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