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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 ( $1.0 \text{ mol dm}^{-3}$  KOH; 298.2K) is  $-578 \text{ kJ mol}^{-1}$ . Hence its enthalpy of formation is  $-1170 \text{ kJ mol}^{-1}$ .

INTRODUCTION

The preparation and properties of tungsten azide pentafluoride,  $\text{WF}_5\text{N}_3$ , 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  $\text{WF}_5\text{N}_3$  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  $1.0 \text{ mol dm}^{-3}$  KOH, using about  $120 \text{ cm}^3$  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  $\text{kJ mol}^{-1}$ . The uncertainties attendant on calibration are  $\pm 4 \text{ kJ mol}^{-1}$  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,  $-578 \text{ kJ mol}^{-1}$ , and the auxiliary data in Table 1, the enthalpy of formation of  $WF_5N_3(s)$  is calculated from the equation

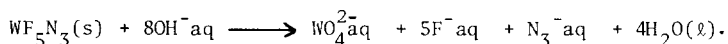


TABLE 1

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

$OH^-aq$	-230 <sup>4</sup>	$N_3(g)$	439 <sup>7</sup>
$H_2O(l)$	-285.8 <sup>4</sup>	$WF_6(g)$	-1723 <sup>8</sup>
$F^-aq$	-335.35 <sup>5</sup>	$W(g)$	837 <sup>9</sup>
$WO_4^{2-}aq$	-1073.2 <sup>6</sup>	$F(g)$	79.39 <sup>5</sup>
$N_3^-aq$	260.1 <sup>4</sup>		

To make an estimate of the strength of the W-N band in  $WF_5N_3$  a value of  $\Delta H_{sol}(WF_5N_3)$  is required; for the present we assume this to be  $35 \text{ kJ mol}^{-1}$ . This gives  $\Delta H_f(WF_5N_3(g)) = -1180 \text{ kJ mol}^{-1}$ , and the enthalpy of the change  $WF_5N_3(g) \rightarrow W(g) + 5F(g) + N_3(g)$  is thence estimated to be  $2853 \text{ kJ mol}^{-1}$ . The enthalpy of the process  $WF_6(g) \rightarrow W(g) + 6F(g)$  is  $3036 \text{ kJ mol}^{-1}$ , giving  $D(W-F) = 506 \text{ kJ mol}^{-1}$  and hence  $D(W-N) \sim 323 \text{ kJ mol}^{-1}$ . 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  $1.84\overset{\circ}{\text{A}}$  [1], near to that in  $WF_6$  vapour ( $1.826\overset{\circ}{\text{A}}$ ) [10]. It is interesting to compare  $D(W-N)$  with  $D(W-Cl)$  in  $WF_5Cl$  and  $WF_4Cl_2$  [2]; similar calculations give  $D(W-Cl) = 397 \text{ kJ mol}^{-1}$  respectively in  $WF_5Cl$  and  $389 \text{ kJ mol}^{-1}$  in  $WF_4Cl_2$ .

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



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

#### ACKNOWLEDGEMENT

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