

Enthalpies of hydrolysis of the xenon complexes $\text{XeF}_2 \cdot \text{VF}_5$, $\text{XeF}_2 \cdot \text{CrF}_4$, $\text{XeF}_2 \cdot \text{MnF}_4$ and $\text{XeF}_6 \cdot \text{CrF}_4$ *

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Abstract

The enthalpies of hydrolysis of the complexes $\text{XeF}_2 \cdot \text{VF}_5$, $\text{XeF}_2 \cdot \text{MnF}_4$ and $\text{XeF}_6 \cdot \text{CrF}_4$ have been measured in alkaline or neutral solution as appropriate. From the experimental results the enthalpies of formation of these complexes can be estimated to be -1664 , -1292 and $-1620 \text{ kJ mol}^{-1}$, respectively. A new value for $\Delta H_f(\text{CrF}_4)(\text{s})$ is proposed ($-1270 \pm 10 \text{ kJ mol}^{-1}$) based on the enthalpies of hydrolysis of CrF_4 . The enthalpies of hydrolysis of $\text{XeF}_2 \cdot \text{CrF}_4$ in neutral and alkaline solutions have also been measured, but it has not been possible to obtain from them a reliable value for its enthalpy of formation.

Introduction

Although a considerable number of complexes between XeF_2 and metal fluorides are known, thermochemical measurements have been confined to complexes with SbF_5 , NbF_5 and TaF_5 [1, 2]. No similar measurements involving complexes of XeF_6 have been reported.

In this communication, we present the results of calorimetric measurements of the hydrolysis of the complexes $\text{XeF}_2 \cdot \text{VF}_5$, $\text{XeF}_2 \cdot \text{CrF}_4$, $\text{XeF}_2 \cdot \text{MnF}_4$ and $\text{XeF}_6 \cdot \text{CrF}_4$. The hydrolysis of CrF_4 has also been studied; the results are used to update von Wartenberg's value for the enthalpy of formation of chromium tetrafluoride [3].

Experimental

Compounds

$\text{XeF}_2 \cdot \text{VF}_5$ was prepared by the reaction between xenon difluoride and an excess of vanadium pentafluoride in a nickel reaction vessel at 90°C

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[4]. $\text{XeF}_4 \cdot \text{VF}_5$ is a colourless solid with a vapour pressure about 0.66 kN m^{-2} at 20°C . $\text{XeF}_2 \cdot \text{CrF}_4$ was synthesised by the reaction between chromium pentafluoride and an excess of xenon difluoride in a Teflon-FEP reaction vessel at 35°C [5]. $\text{XeF}_2 \cdot \text{CrF}_4$ is a blue nonvolatile solid at room temperature. $\text{XeF}_2 \cdot \text{MnF}_4$ was synthesised using the reaction between manganese difluoride and xenon difluoride in a nickel reaction vessel at 120°C [6]. $\text{XeF}_2 \cdot \text{MnF}_4$ is a red nonvolatile solid at room temperature. $\text{XeF}_6 \cdot \text{CrF}_4$ was synthesised using either the reaction between chromium difluoride and xenon hexafluoride at 120°C or the reaction between chromium pentafluoride and xenon hexafluoride at 60°C ; $\text{XeF}_6 \cdot \text{CrF}_4$ is brick-red nonvolatile solid at room temperature. CrF_4 was prepared by a fluoride-ion capture method [8] from $\text{XeF}_6 \cdot \text{CrF}_4$ in anhydrous hydrogen fluoride using the strong fluoride ion acceptors AsF_5 and/or BF_3 [5, 7]. CrF_4 is a violet-blue solid compound with negligible vapour pressure at room temperature.

The complexes prepared were pure, and fully characterised by chemical analysis, vibrational spectroscopy, magnetic susceptibility and X-ray powder photography. CrF_4 prepared by the above method was found to contain 2% by weight of $\text{XeF}_6 \cdot \text{CrF}_4$.

Calorimetric measurements

All the compounds investigated are extremely moisture-sensitive, so transfer into 1 ml Pyrex containers was made in a dry-box for the nonvolatile samples and on a vacuum line for $\text{XeF}_2 \cdot \text{VF}_5$. In all cases, containers were pretreated with elemental fluorine. No significant hydrolysis of the compounds was observed before the bulbs were broken in the calorimeter. Samples of between 30 and 80 mg were used with 30 ml of the appropriate aqueous hydrolysing medium. Measurements were made using an LKB 8700 calorimeter (Bromma, Sweden) with ancillary apparatus as described earlier [9]. The ranges of error reported in Tables 1 and 2 refer to 90% confidence limits for the mean values given.

TABLE 1

Enthalpies of hydrolysis of compounds (in kJ mol^{-1})

Compound	$\Delta H(\text{hydr.})/\text{H}_2\text{O}$	$\Delta H(\text{hydr.})/\text{OH}^-$
$\text{XeF}_2 \cdot \text{VF}_5$		-931.3 ± 10.0 (5) ^b
$\text{XeF}_2 \cdot \text{CrF}_4$	-242.9 ± 7.7 (6) ^a	-794.4 ± 10.0 (6) ^b
$\text{XeF}_2 \cdot \text{MnF}_4$		-716.2 ± 15.7 (5) ^b
$\text{XeF}_6 \cdot \text{CrF}_4$	-661.2 ± 7.4 (6)	-1395.2 ± 20.0 (5) ^b
CrF_4	-149.4 ± 5.4 (6)	-362.0 ± 10.0 (5) ^c
	-151 ± 5.5 (6)	-366.9 ± 10.2 (5) ^{cd}

^aThe number of determinations is given in parentheses.

^bIn 0.1 M KOH.

^cIn 1.0 M KOH.

^dCorrected for a 2% $\text{XeF}_6 \cdot \text{CrF}_4$ impurity.

TABLE 2

Ancillary data relating to compounds studied (in kJ mol⁻¹)^a

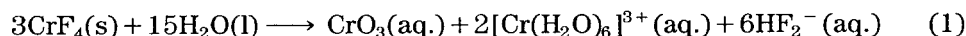
ΔH_f^0		ΔH_f^0		ΔH_f^0	
F ⁻ (aq.)	-335.35	OH ⁻ (aq.)	-229.99	Cr(OH) ₃ (ppt.)	-1064.0
HF(aq.)	-322.8	Xe(aq.)	-17.8	CrO ₄ ²⁻ (aq.)	-881.15
HF ₂ ⁻ (aq.)	-655.4	HVO ₄ ²⁻ (aq.)	-1159.0	[Cr(H ₂ O) ₆] ³⁺ (aq.)	-1999.1
H ₂ O(l)	-285.83	CrO ₃ (aq.)	-602.2	MnO ₂ (ppt.)	-502.5
XeO ₃ (aq.)	+413				

^a ΔH_f^0 [F⁻(aq.)] from ref. 10; other values from ref. 11. ΔH_f^0 [HF(aq.)] and ΔH_f^0 [HF₂⁻(aq.)] have been recalculated to a base of ΔH_f^0 [F⁻(aq.)] = -335.35 from the base of -332.63 kJ mol⁻¹ [11].

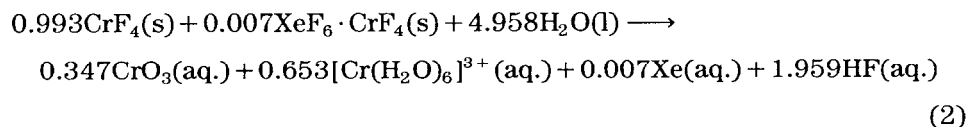
Results and discussion

Chromium tetrafluoride

In aqueous solution, Cr^{IV} disproportionates to Cr^{III} and Cr^{VI}. In water, the ideal hydrolysis scheme is:



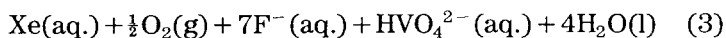
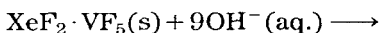
In the presence of 2% by weight of XeF₆·CrF₄, eqn. (1) is modified to:



and we have assumed this to be the actual course of the reaction. Using the data in Tables 1 and 2, allowing for dilution effects for HF(aq.) and Xe(aq.), and taking ΔH_f (XeF₆·CrF₄) = -1620.4 ± 8.0 kJ mol⁻¹ (see below), the enthalpy of formation of CrF₄ is estimated to be -1270.5 ± 10 kJ mol⁻¹. A check from the similar alkaline hydrolysis yields ΔH_f (CrF₄)(s) = -1295 kJ mol⁻¹. This figure is believed to be less reliable than the former because of the uncertainty of the Cr^{III} species formed; it has been assumed, for the purposes of calculation, to be Cr(OH)₃. These figures compare with a value from von Wartenberg's experiments of -1258 ± 15 (approx.) kJ mol⁻¹ (recalculated for ΔH_f [F⁻(aq.)] = -335.35 kJ mol⁻¹ [10] from the NBS data for CrF₄ based on ΔH_f [F⁻(aq.)] = -332.63 kJ mol⁻¹ [11]). It should be mentioned that von Wartenberg's experiment was very different from ours; it depended on the (incomplete) hydrogen reduction of CrF₄ to CrF₃, whose enthalpy of formation was in turn determined by the reduction to Cr metal by Mg. The agreement between the two sets of data is remarkably good, and we suggest a working value for ΔH_f (CrF₄)(s) of -1270 ± 10 kJ mol⁻¹.

XeF₂·VF₅

The alkaline hydrolysis in 0.1 M KOH is believed [cf. refs. 1, 12–14] to take place according to the equation:

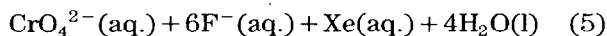
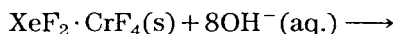
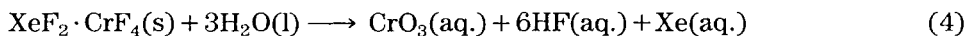


and the enthalpy of formation of $\text{XeF}_2 \cdot \text{VF}_5$ is accordingly estimated to be $-1664 \pm 11.0 \text{ kJ mol}^{-1}$. It follows that the complex is formed exothermally from $\text{XeF}_2(\text{s})$ ($\Delta H_f = -162.8 \text{ kJ mol}^{-1}$ [15] and $\text{VF}_5(\text{l})$ ($\Delta H_f = -1482.2 \text{ kJ mol}^{-1}$) [12]; this result is in accord with the existence of the complex in the vapour state.

The available data [2] indicate that $\text{XeF}_2 \cdot \text{TaF}_5$ is also formed exothermally from its two starting fluorides, whereas $\text{XeF}_2 \cdot \text{NbF}_5$ is formed endothermally and is clearly a very unstable material. A factor which may in part account for the comparative stability of the VF_5 complex is the strength of fluorine bridging in NbF_5 and TaF_5 compared with that in VF_5 [16].

XeF₂ · CrF₄

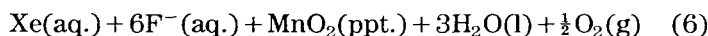
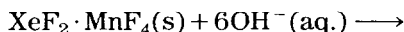
Xe^{II} is a sufficiently strong oxidising agent to convert Cr^{IV} quantitatively into Cr^{VI} . Hydrolyses are in accord with the following equations, for neutral and alkaline solutions respectively:



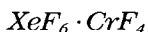
The calculated enthalpies of formation of the complex, at -1455 and $-1418 \text{ kJ mol}^{-1}$ respectively, are too far apart for much reliance to be placed on either value; in consequence it is not possible from the present measurements to comment on the stability of $\text{XeF}_2 \cdot \text{CrF}_4$ with respect to its components.

XeF₂ · MnF₄

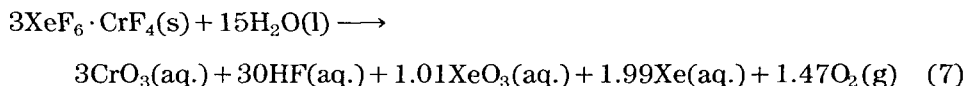
Hydrolysis of $\text{XeF}_2 \cdot \text{MnF}_4$ yields hydrated MnO_2 and O_2 is evolved. No MnO_4^- appears in dilute H_2SO_4 solutions and MnO_4^{2-} is not formed in appreciable proportions in alkaline solution unless the alkali is about 15 M or stronger. In 0.1 M KOH the hydrolysis appears to be in accord with the following scheme [17]:



The enthalpy of formation of the complex, calculated from the enthalpy of hydrolysis (Table 1), is $-1292 \pm 16 \text{ kJ mol}^{-1}$. This value indicates that $\text{XeF}_2 \cdot \text{MnF}_4$ is formed exothermally from $\text{XeF}_2(\text{s})$ ($\Delta H_f = -163 \text{ kJ mol}^{-1}$) and $\text{MnF}_4(\text{s})$ ($\Delta H_f = -1080 \pm 15 \text{ kJ mol}^{-1}$ [17]), in accord with its known stability [6].



The hydrolysis of this complex is very violent, both in neutral and alkaline solutions, and is accompanied by flashes of light. It would seem ideally that all the Xe^{VI} remaining after dissolution in water should appear as Xe^{VI} [18], but titration of solutions under the present conditions of hydrolysis indicates some of the $\text{XeO}_3(\text{aq.})$ is decomposed to Xe and O_2 . The hydrolysis equation is therefore assumed to be:



Allowing for the dilution of the $\text{HF}(\text{aq.})$ and $\text{Xe}(\text{aq.})$ under our conditions, $\Delta H_f(\text{HF})(\text{aq.})$ is $-323.7 \text{ kJ mol}^{-1}$ and $\Delta H_f(\text{Xe})(\text{aq.})$ is $-16.0 \text{ kJ mol}^{-1}$; using these figures and the data in Table 2 the enthalpy of formation of $\text{XeF}_6 \cdot \text{CrF}_4$ is estimated to be $-1620.4 \pm 8.0 \text{ kJ mol}^{-1}$. It is not possible to estimate a value for ΔH_f from the alkaline hydrolysis, because the nature and number of the Xe species remaining in solution is unknown. The value of 1620 kJ mol^{-1} implies that the compound has a small negative enthalpy of formation from the two constituent fluorides ($\Delta H_f = -338 \text{ kJ mol}^{-1}$ for $\text{XeF}_6(\text{s})$ [13] and $-1270 \text{ kJ mol}^{-1}$ for CrF_4).

At present there is not sufficient information on $\text{XeF}_6 \cdot \text{CrF}_4$ to compare with this thermochemical evidence, though it should be noted the compound appears to be stable up to 30°C . The chief value of the present work is that it indicates that it is possible to obtain reasonably reliable thermochemical data from hydrolysis measurements on XeF_6 complexes in spite of the violence of their reactions with water, a conclusion confirmed by the measurement of the enthalpy of hydrolysis of $\text{XeF}_6 \cdot \text{BF}_3$ [19].

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