SOLUTION CHEMISTRY OF COBALT IN LIQUID HYDROGEN FLUORIDE

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SUMMARY

Cobalt(II) fluoride dissolves in HF in the presence of excess BF₃ or AsF₅: solid adducts are isolable from these solutions. Insoluble CoF_3 decomposes to cobalt(II) under the same conditions. The CoF_6^{3-} is solvolysed by HF except in the presence of excess F⁻. Cs₂CoF₆ is soluble in HF but the solutions decompose above $10^{\circ}C$ yielding F₂; such solutions are powerful fluorinating agents and convert MnF₃ to MnF₆²⁻ and Xe to XeF₂.

INTRODUCTION

Fluorine compounds of cobalt(III) and -(IV), such as CoF_3 , K_3CoF_6 and Cs_2CoF_6 , are thermally stable solid materials [1]. These compounds have no aqueous chemistry on account of their high lattice energies, sensitivity to hydrolysis and the oxidising ability of cobalt in these oxidation states. The use of anhydrous HF as a solvent for such compounds seemed promising in view of its favourable physical and chemical properties [2]; of these the excellent redox characteristics of the pure solvent are especially important. This report describes the results of experiments performed in transparent, fluorocarbon polymer apparatus and gives more details than were given in our earlier preliminary communication [3].

RESULTS AND DISCUSSION

Cobalt(II) fluoride, a pale pink, air-stable, paramagnetic (μ_{eff} 4.6BM at 300[°]K) solid, is essentially insoluble in anhydrous HF[4]. In the presence of KF we found no significant change in the solubility of Co^{II}. On the basis of its reactions with BF₃ and AsF₅, KCoF₃ behaves similarly and is solvolysed in HF according to:

$$\mathsf{KCoF}_3 \xrightarrow{\mathrm{HF}} \mathsf{CoF}_2 + \mathsf{K}^+ + \mathsf{F}^-$$

When a suspension of CoF_2 in HF is treated with BF_3 or AsF_5 the pink solid dissolves gradually to form a cherryred solution (λ_{max} at 18500 and 20750 (sh) cm⁻¹) confirming that Co(II) is present in solution. KCoF₃ reacts with HF/BF₃ to give a white precipitate KBF₄ and a cherry-red solution. Analysis for cobalt in the unstable residue left after evaporating the red solution to dryness was consistent with the formulation $\text{CoF}_2.\text{BF}_3$

Analysis: Found: Co,35.4%. CoF₂.BF₃ requires Co, 35.77%.

Found: Co,21.9%. CoF_2 .AsF₅ requires Co 22.08%. The stronger fluoride ion acceptor SbF₅ was observed to give rise to an HF-soluble Co^{II} fluoroantimonate. These adducts have also been prepared by Dean from Co and AsF₅(SbF₅) in liquid SO₂ [5].

Clifford <u>et al.</u> [6] reported that AsF_5 did not bring either CoF_2 or CuF_2 into solution in HF: their AsF_5 had been made by the action of ClF_3 on a suspension of As in HF. In our work we find that AsF_5 does form HF-soluble fluoroarsenates of both Co^{II} and Cu^{II} [7]. Although we did not attempt to repeat Clifford <u>et al.</u>'s work we did examine the action of ClF_3 on antimony in HF. In a vigorous reaction $[ClF_2]$ [SbF₆] was produced; it could be crystallised from the medium and characterised by Raman spectroscopy (bands at 275,290,540,640 and 812 cm^{-1}) When CoF_2 was treated with $[ClF_2]$ [SbF₆] in HF no coloured solution was produced, however the residue was found to

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be CoF_3 , on the basis of Co and F analyses. Since $\left[\operatorname{ClF}_2\right]\left[\operatorname{AsF}_6\right]$ has been reported to be a stable compound [8] it seems likely that Clifford <u>et al</u>. used a solution of this rather than AsF_5 in HF for the reactions with CoF_2 and CuF_2 .

Cobalt(III) fluoride, a buff coloured, paramagnetic (μ_{eff} 2.5BM at 300[°]K) solid, was found to be virtually insoluble in anhydrous HF in agreement with earlier reports [4]. It did gradually dissolve after excess BF₃ had been added; a reaction time of 12h was needed for gram quantities at room temperature. However, the cherry-red solution produced contained Co^{II} and CoF₂.BF₃ was isolated. No reaction took place between CoF₃ and AsF₅ in HF over the same period unless a reducing agent (e.g. SO₂) was present.

The pale blue, paramagnetic (μ_{eff} 5.6BM) complex fluoride, $K_3 \text{CoF}_6$, was found to be insoluble in HF although reaction did take place as shown by the brown colour of the residue. This solid was filtered off, washed once with HF, dried <u>in</u> vacuo, and analysed. Found: Co, 32.8; F, 43.4%, Co oxidation state 2.94. CoF₃ requires Co, 50.85; F 49.15%. Co oxidation state 3.0. KCoF₄ requires Co, 33.86; F 43.67%, Co oxidation state 3.0. Prolonged and repeated (ten times) washing of the residue left a buff coloured solid which analysed correctly for CoF₃. Found: Co, 50.7; F, 47.8%. These results are consistent with the stepwise solvolysis of the starting material, thus:

 $K_3CoF_6 \longrightarrow KCoF_4 + 2K^+ + 2F \longrightarrow CoF_3 + 3K^+ + 3F$. The proposed intermediate $KCoF_4$ corresponds to a known phase [9], more recently used as a mild fluorinating agent for organic compounds. Mixtures containing KF and K_3CoF_6 in the molar proportions of 2.3:1, 5.2:1 and 9.8:1 were treated with anhydrous HF at room temperature. The first two samples gave colourless solutions and a pale blue solid phase, which was identified as K_3CoF_6 from its X-ray powder pattern. Thus it would appear that $\operatorname{CoF}_6^{3-}$ is not solvolysed by HF containing excess F at an appropriate concentration. The third sample was treated similarly and gave a pale blue solution (λ_{\max} at 14,500 and 11,500 cm⁻¹) as well as a blue solid. Since CoF₃ was found to react with excess KF in HF in an analogous manner the solvolysis of this hexafluoroanion is seen to be entirely reversible. Manganese(III) fluoride and MnF₆³⁻ are also readily interconverted under similar conditions [7]although no evidence for the production of MnF₄³⁻ salts as intermediates was obtained. On the other hand NiF₆³⁻ undergoes a disproportionation reaction in HF [10].

Although CoF_3 is formed from CoF_2 and F_2 at 150° C we obtained evidence that ClF_3 , or rather $\left[\operatorname{ClF}_2\right] \left[\operatorname{SbF}_6\right]$, converts CoF_2 to CoF_3 in HF at room temperature. It was therefore to be expected that F_2 should be capable of effecting the same oxidation. Caesium fluoride and CoF_2 in a lo:1 molar ratio were treated with HF and then F_2 at a modest pressure (ca. 400mm): the pink CoF_2 turned brown and, finally, pale blue. The supernatant also became blue but no further changes occurred under these conditions. The blue solid and solution were shown to contain Co(III) by iodimetry/cobalt analysis and visible spectroscopy.

There was no evidence for the oxidation of cobalt(III) to cobalt(IV) under these conditions. However, Cs_2CoF_6 , an orange-yellow solid, μ_{eff} 2.79BM at 300°K, can be prepared from Cs_2CoCl_4 and F_2 at 300°C[7]. This cobalt(IV) complex was prepared and characterized and its solution properties in HF were examined. At -80°C the complex dissolved to form a dark red solution. At 10°C the solution began to decompose, the colour of the solution fading over a period of $\frac{1}{2}h$, a gas was evolved and a greybrown solid was deposited. This solid was filtered, washed once with HF and dried. Analysis: Co 39.4%; F 43.7%; Co oxidation state 3.24 corresponding to the approximate

composition $Cs_{0.2}CoF_{3.4}$. The gas evolved reacted with excess mercury at 20 °C to give Hg_2F_2 only; this product was identified from its X-ray powder diffraction pattern (tetragonal, a = 3.66, c = 10.9^A.) Under these conditions this reaction is typical of F₂ but not of OF₂. Serious attack on the walls of the PCTFE vessel in contact with the solution was found to have taken place. These results clearly demonstrate that $\operatorname{CoF}_6^{2-}$ is unstable in liquid HF at room temperature with respect to the formation of F, and some mixed Co(III)/Co(IV) solid product. The colour of the Co(IV) solution appeared to be different from that of the solid complex; this observation could not be confirmed by spectroscopic measurements owing to interference from the decomposition reaction. However, it is consistent with a change in the environment of the cobalt due, for example, to solvolysis to CoF_5 . This is supported by the fact that the rate of decomposition of the Co(IV) solution was slowed by a factor of four by the addition of excess CsF to the solution. Moreover, the addition of $\ensuremath{\mathsf{AsF}}_{\mathsf{F}}$ to a Co(IV) solution in HF at below -50°C caused immediate decomposition to form CoF3, 2CsAsF6 and F2.

The reactivity of these unstable solutions of cobalt(IV) in HF was also explored. Hydrogen fluoride was added to a 1:1 mixture of MnF₃ and Cs₂CoF₆ at low temperature; after ca 15 min. at 20[°]C the reaction had finished, the yellow solution was filtered and evaporated to dryness. From X-ray powder photography Cs_2MnF_6 (<u>a</u> = 8.92Å) was shown to be present. No such redox reaction was found to take place between MnF3 and K3CoF6 in HF. Xenon and Cs2CoF6 were allowed to react in the presence of liquid HF at room temperature for ¹/₂h. The volatiles, HF, unreacted Xe and some F_2 , were removed at $-60^{\circ}C$ in vacuo and pumped away: the less volatile materials were transferred at +60° to a PCTFE n.m.r. tube. Additional HF was introduced and the 19 F n.m.r. spectrum was recorded at -20 $^{\circ}$ C: a resonance at +2.9 ppm, relative to the HF resonance with $J(^{129}Xe - ^{19}F) = 5600Hz$, was taken as evidence that XeF₂

had been produced [11]. A very weak resonance observed at -173ppm was tentatively assigned to XeF_{A} [11].

Although F_2 is also produced during these redox reactions it is expected as a decomposition product from the unstable $\operatorname{CoF_6}^{2-}$. However Xe and F_2 do not react in the dark at a significant rate at 20° C and, therefore, we infer that Co(IV) oxidises Xe by a direct, electron transfer or radical mechanism. Both $K_2\operatorname{NiF_6}$ and $K_3\operatorname{CuF_6}$ are able to oxidise Xe to XeF₂ under similar conditions [7]; NiF₆²⁻ does not generate F_2 in HF at 20° C and is therefore the most efficient of the three oxidising agents because of its greater kinetic stability towards solvent attack.

The above experiments, although only qualitative in nature, also show that CoF_2 behaves as a weak F ion donor, i.e. as a base, in HF, whereas CoF_3 is a weak F ion acceptor. In addition it seems unlikely that CoF_4 can be prepared by the low temperature solvolysis of Cs_2CoF_6 in HF.

EXPERIMENTAL

Materials

Hydrogen fluoride (I.C.I. anhydrous grade) was purified by vacuum transference in a fluorocarbon vacuum manifold [7]. Fluorine was generated electrochemically in a 60A cell, provided by the Imperial Chemical Industries Ltd.; AsF_5 , ClF_3 , CoF_3 , K_3CoF_6 and Cs_2CoF_6 were prepared by direct fluorination of As, Cl_2 , $CoCl_2$, $K_3Co(CN)_6$ and Cs_2CoCl_4 respectively in a stream of F_2 and dry N₂ at appropriate temperatures. BF_3 (Imperial Smelting Corporation) was used directly from the cylinder. Anhydrous HI required for iodimetric work was prepared by the reaction of anhydrous KI and liquid HF in a twolimbed Kel-F reactor [12]: the HI, along with a trace of HF was distilled from one limb onto the fluorometallate in the other.

Apparatus

Most of the work was carried out with a PCTFE vacuum manifold constructed in the Departmental Workshops at Nottingham University. The PCTFE reaction tubes were bought from the Argonne National Laboratories, Illinois, U.S.A.; a small Teflon-FEP (Du Pont) reaction tube of similar dimensions was machined out of a solid block of the polymer. Reactions in HF (ca 5 ml) were carried out on approximately 2 mmol samples of the fluorides in sample tubes that had been previously washed out with liquid HF. All moisture-sensitive solids were handled in an inert atmosphere box, filled with dry N₂ gas which was recirculated over molecular sieves.

Analysis

Cobalt and fluoride were determined by EDTA/murexide titration and PbClF precipitation. Oxidation states were obtained by aqueous iodimetry after reduction with anhydrous HI. X-ray powder photographs were obtained using filtered molybdenum or copper radiation with a Philips lOcm camera. Magnetic susceptibilities were measured at room temperature by the Gouy method. The u.v.-visible spectra were recorded on either a SP700 or a SP800 (Unicam) instrument: diffuse reflectance attachments were available for both instruments; solution spectra were measured on samples in 6mm tubing.

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