METAL (II) HEXAFLUOROARSENATES: THERMAL DECOMPOSITION
STUDIES ON THE ADDUCTS $MF_2 \cdot 2AsF_5$ (M = Mg, Ca, Sr, Mn,
Co, Ni, Cd, Hg, Pb), $2MF_2 \cdot 3AsF_5$ (M = Fe, Cu, Zn) and
$MF_2 \cdot AsF_5$ (M = Ag, Sn)

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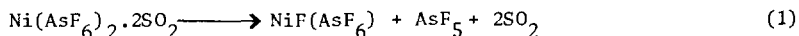
SUMMARY

Thermal studies have shown that metal(II) hexafluoro-arsenates
of the types $MF_2 \cdot 2AsF_5$ (M = Mg, Ca, Sr, Mn, Co, Ni, Cd, Hg, Pb),
$2MF_2 \cdot 3AsF_5$ (M = Fe, Cu, Zn) and $MF_2 \cdot AsF_5$ (M = Ag, Sn), prepared by
the reaction of metal difluorides with AsF_5 in anhydrous HF at room
temperature, decompose when heated in an argon atmosphere. In all
cases AsF_5 is given off. For some of the adducts the decompositions
proceed in one or more steps to give the original difluorides, but
for others, the decompositions overlap one another. The greatest
range of intermediate stoicheiometries results from the decompositions
of the $MF_2 \cdot 2AsF_5$ type adducts in which the metal difluoride content
is a minimum. In decompositions of adducts of this type as many as
three different intermediates, $2MF_2 \cdot 3AsF_5$, $MF_2 \cdot AsF_5$ and $2MF_2 \cdot AsF_5$,
may be observed.

INTRODUCTION

Many examples of metal(II) difluoride adducts with arsenic penta-
fluoride have recently been produced by the reactions of the metal
difluorides with AsF_5 in anhydrous HF [1,2]. The adducts fall into
four different classes represented by the formulae, $MF_2 \cdot 2AsF_5$,
$2MF_2 \cdot 3AsF_5$, $MF_2 \cdot AsF_5$ and $2MF_2 \cdot AsF_5$. Two of these adduct types have
stoicheiometries analogous to those for noble-gas difluoride adducts,
$NgF_2 \cdot AsF_5$ and $2NgF_2 \cdot AsF_5$ (Ng = Kr, Xe). For these krypton and xenon

species it is well documented that the 1:1 compounds readily lose AsF_5 to yield the 2:1 adducts [3-5].

In addition to the recent reports of metal(II) hexafluoroarsenates, earlier papers include reference to $MnF_2.2AsF_5$ [6], $NiF_2.2AsF_5.2SO_2$ [7], and $MF_2.AsF_5$ (Fe [6], Co [8], Ni [6,7], Sn [9,10]). However, only in the cases of the manganese, cobalt, and nickel species were any references made to the tendency of any of the adducts to lose AsF_5. Qualitatively it was noted that the 'normal' adducts [i.e. $M^{II}(AsF_6)_2$] decompose to the fluorobasic species [i.e. $MF(AsF_6)$] [6] and a quantitative study was carried out for the nickel compound (equation 1) [7].

$$Ni(AsF_6)_2.2SO_2 \longrightarrow NiF(AsF_6) + AsF_5 + 2SO_2 \qquad (1)$$

This paper summarizes the results of thermal studies on a wide range of metal(II) hexafluoroarsenates of the types $MF_2.2AsF_5$, $2MF_2.3AsF_5$ and $MF_2.AsF_5$. In the cases of the adducts $2MF_2.3AsF_5$ (M = Fe, Cu, Zn) and $SnF_2.AsF_5$ the intermediate products were isolated and characterized fully by chemical analysis, vibrational spectroscopy and X-ray diffraction studies.

RESULTS AND DISCUSSION

Of the known metal(II) hexafluoroarsenates those containing the largest proportion of AsF_5 can be represented by the general formula $MF_2.2AsF_5$ [1]. Since adducts of composition $2MF_2.3AsF_5$, $MF_2.AsF_5$ and $2MF_2.AsF_5$ have also been identified [2], and since some of these compounds have been obtained by the thermal diss- ociation of the more arsenic pentafluoride-rich adducts, it is reasonable to expect that under ideal conditions thermal decomp- ositions of the adducts might proceed stepwise through the sequence $MF_2.2AsF_5$, $2MF_2.3AsF_5$, $MF_2.AsF_5$, $2MF_2.AsF_5$ to MF_2.

The results of our thermal dissociation studies, carried out in an argon atmosphere on a Mettler Thermoanalyser, are summarized in Table 1.* Details of the decomposition of representatives of each class are presented and discussed below.

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* It should be noted that temperatures quoted in the Table refer to the decompositions under dynamic thermal conditions. If the decompositions are carried out under static equilibrium conditions the decomposition temperatures may be significantly lower.

TABLE 1

Summary of thermal decomposition schemes for metal(II) hexafluoroarsenates

$SrF_2.2AsF_5$ —[70 – 352°C; DTA 330°C end; DTG 340°C]→ $SrF_2.AsF_5$ —[352 – 475°C; DTA 380°C end; DTG 380°C]→ SrF_2

$PbF_2.2AsF_5$ —[64 – 165°C; DTA 154°C end;DTG 154°C]→ $2PbF_2.3AsF_5$ —[165 – 211°C; DTA 198°C end; DTG 198°C]→ $2PbF_2.AsF_5$ —[226 – 431°C; DTA 401°C end;DTG 401°C]→ $PbF_2.AsF_5$ —[431 – 680°C; DTA 469°C end;DTG 469°C]→ PbF_2

$CaF_2.2AsF_5$ —[60 – 312°C; DTA 298°C end]→ $CaF_2.AsF_5$ —[312 – 450°C; DTA 335°C end; DTG 335°C]→ CaF_2

$MnF_2.2AsF_5$ —[105 – 240°C; DTA 192°C end; DTG 192°C]→ MnF_2

$CdF_2.2AsF_5$ —[105 – 173°C; DTA 173°C end; DTG 173°C]→ $CdF_2.AsF_5$ —[173 – 352°C; DTA 202°C end; DTG 202°C]→ CdF_2

$HgF_2.2AsF_5$ —[65 – 95°C; DTA 85°C end; DTG 85°C]→ $HgF_2.AsF_5$ —[95 – 430°C; DTA 170°C, 210°C end; DTG 160°C, 210°C]→ HgF_2

$MgF_2.2AsF_5$ —[65 – 700°C; DTA 192°C end; DTG 192°C]→ MgF_2

$CoF_2.2AsF_5$ —[70 – 150°C; DTA 120°C end;DTG 120°C]→ $(2CoF_2.3AsF_5?)$ —[115 – 150°C]→ $(CoF_2.AsF_5)$ — complex decomposition

$NiF_2.2AsF_5$ —[60 – 115°C; DTA 88°C end;DTG 83°C]→ $2NiF_2.3AsF_5$ —[115 – 150°C; DTA 147°C end;DTG 153°C]→ $NiF_2.AsF_5$ —[150 – 600°C; DTA 167°C end; DTG 167°C]→ NiF_2

$2FeF_2.3AsF_5$ —[70 – 150°C; DTA 123°C end;DTG 120°C]→ $FeF_2.AsF_5$ —[150 – 300°C; DTA 194°C, 210°C end; DTG 194°C, 210°C]→ FeF_2

$2CuF_2.3AsF_5$ —[69 – 118°C; DTA 114°C end;DTG 114°C]→ $CuF_2.AsF_5$ —[118 – 400°C; DTA 170°C end; DTG 168°C]→ CuF_2

$2ZnF_2.3AsF_5$ —[58 – 125°C; DTA 85°C end;DTG 103°C]→ $ZnF_2.AsF_5$ —[125 – 300°C; DTA 150°C end; DTG 150°C]→ ZnF_2

$SnF_2.AsF_5$ —[79 – 215°C; DTA 204°C end; DTG 200°C]→ $2SnF_2.AsF_5$ —[235 – 275°C; DTA 252°C ex; DTG 252°C]→ SnF_2

$AgF_2.AsF_5$ —[65 – 355°C; DTA 175°C end;DTG 175°C]→ $2AgF_2.AsF_5$ —[352 – 600°C; DTA 485, 494, 548°C end; DTG 485, 498, 577°C]→ AgF_2

end.: endothermic peak of DTA curve
ex.: exothermic peak of DTA curve

Decompositions of the $MF_2 \cdot 2AsF_5$ adducts

In this class three district structural types occur and their structures have been tentatively rationalized in terms of the size of the metal ion in the difluoride. The strontium and lead adducts belong to the first of these structural types with a metal ion radius of about 1.3 Å. However, their decompositions are not identical. The strontium adduct decomposes to the difluoride in two steps which may well be due to the occurrence of firstly Sr^{2+} in the starting material and then SrF^+ ions in the decomposition inter-mediate, $SrF_2 \cdot AsF_5$. Lead, on the other hand, not only has a well-defined cation chemistry but polymeric species in lead compounds are also known and it may well be that combinations of Pb^{2+} and PbF^+ ions in the lattice permit the more ready formation of species such as $Pb^{2+}PbF^+(AsF_6^-)_3$ and $PbF^+F^-PbF^+AsF_6^-$ and hence a four step decomposition is possible (Figure 1 and Table 1).

The decomposition of $PbF_2 \cdot 2AsF_5$ begins at $64^\circ C$. In the first step the sample loses 14.6% of its weight corresponding to a loss of half a mole of AsF_5 per mole of starting material (theoretical weight loss is 14.52%). The step is accompanied by an endothermic effect which gives rise to a DTA peak at $154^\circ C$, and the DTG curve exhibits a peak at the same temperature (Figure 1). In the temper-ature interval between 165 and $211^\circ C$ a further 17.9% weight-loss occurs and this is again accompanied by endothermic DTA and DTG peaks at $198^\circ C$. The combined weight loss for the two steps amounts to 32.5% of the initial sample weight (theoretical value, 29.04%) and corresponds to a loss of 1 mole of AsF_5 per mole of $PbF_2 \cdot 2AsF_5$. This intermediate is rather stable up to $300^\circ C$. Although decomp-osition begins at $226^\circ C$, it is very slow indeed until the temper-ature reaches $300^\circ C$. Between 300 and $431^\circ C$ AsF_5 is lost rapidly and the decomposition is again accompanied by endothermic DTA and DTG peaks at $401^\circ C$. The weight loss for the three steps is 49.7% (c.f. 43.56% theoretical). This discrepancy between the theo-retical and calculated weight loss indicates overlap of the third and final decomposition steps. However, the overall rate of weight loss for the last step is slow. The decomposition is accompanied by another small endothermic DTA and DTG peak at $469^\circ C$. The cumulative weight loss is 57.3% which correlates well with the theoretical value (58.08%) for loss of two moles of AsF_5.
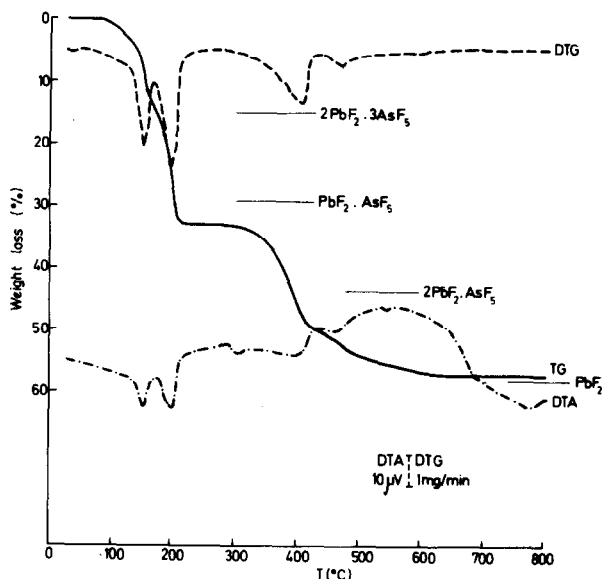
Figure 1: TG, DTG and DTA Curves for the Decomposition of $PbF_2.2AsF_5$

The calcium, manganese, cadmium and mercury adducts constitute a second class in which the radius of the divalent cation is close to 1 Å. The adducts containing Group II metals all decompose as expected to give, first, $MF_2.AsF_5$ type adducts and then the difluoride (Table 1). For manganese, however, the decomposition behaviour is exceptional, it being an example of an adduct which decomposes to the difluoride in a single step (Figure 2). The decomposition begins at $105°C$ and, up to $240°C$, the sample loses 77.9% of its initial weight which agrees well with the expected weight change (78.52%) where two moles of AsF_5 are lost. The DTA curve exhibits two endothermic peaks; a small one at $152°C$ and a strong one at $192°C$ which is at a temperature coincident with the minimum of the DTG curve.

The third class contains the magnesium, cobalt and nickel adducts. Here again the structures are related, the effective ionic radius of the dipositive cation being about 0.7 Å in each case. However, the decomposition routes differ significantly. The adduct containing the Group II element, magnesium, decomposes in a single step. However, $CoF_2.2AsF_5$ has been observed to produce different intermediates and it is clear that its decomposition is complex and not fully understood. The nickel difluoride adduct $NiF_2.2AsF_5$, decomposes through the two intermediates $2NiF_2.3AsF_5$ and $NiF_2.AsF_5$.

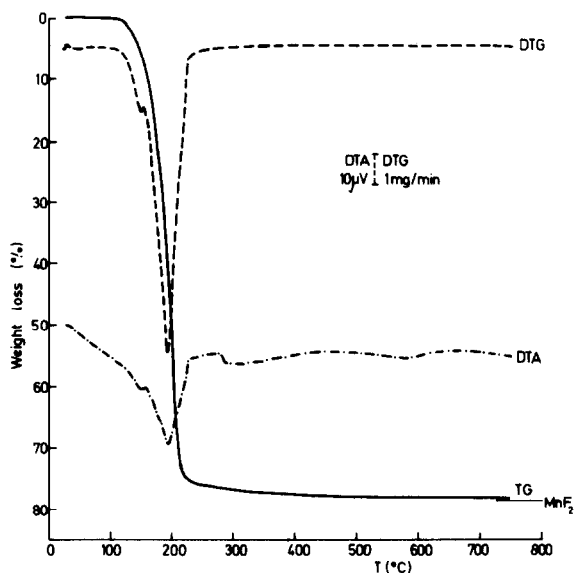Figure 2: TG, DTG and DTA Curves for the Decomposition of $MnF_2 \cdot 2AsF_5$

Decomposition of the $2MF_2 \cdot 3AsF_5$ adducts

The decompositions of these compounds all follow the same pattern and the behaviour of the copper adduct is entirely representative. Decomposition occurs via the $CuF_2 \cdot AsF_5$ adduct to CuF_2 (Figure 3 and Table 1). The sample loses 21.0% of its weight between 69 and 118°C, corresponding to loss of one AsF_5 unit per $2CuF_2 \cdot 3AsF_5$ unit (theoretical value is 23.81%). The step is accompanied by peaks in the DTA and DTG curves at 114°C Further decomposition occurs immediately after the first step and is complete at 200°, the DTA and DTG curves displaying peaks at 168 and 170°C respectively. Beyond 200°C weight loss is slow, the decomposition being complete at 500°C. The overall weight loss of 71.6% of the starting weight is very close to the theoretical value (71.7%) associated with the loss of all the AsF_5.

Only one other of this series of compounds requires further comment in that the first step in the decomposition of $2ZnF_2 \cdot 3AsF_5$ is less well defined than in the cases of the other difluorides because it is overlapped by the second.
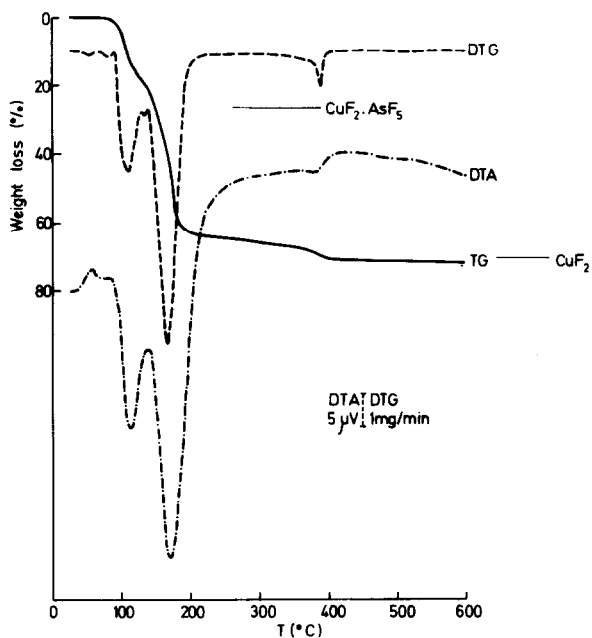
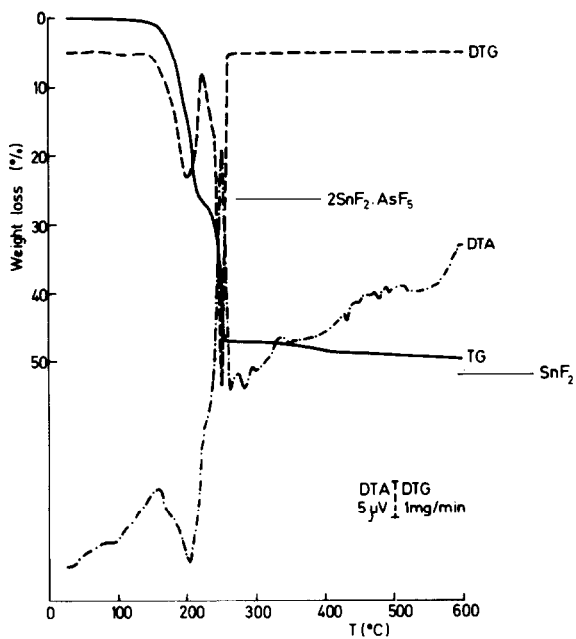Figure 3: TG, DTG and DTA Curves for the Decomposition of $2CuF_2 \cdot 3AsF_5$

Figure 4 : TG, DTG and DTA Curves for the Decomposition of $SnF_2 \cdot AsF_5$

Decompositions of the $MF_2.AsF_5$ adducts

The thermal decompositions of two $MF_2.AsF_5$ adducts, the tin and the silver containing compounds, have been studied (Table 1). In both cases thermal decomposition results in the formation of the intermediate, $2MF_2.AsF_5$. The final residue in the decomposition of the tin compound is SnF_2, but, for $2AgF_2.AsF_5$, metallic silver and AgF were found in the end product rather than AgF_2. The well recognized fluorinating properties of AgF_2 and the fact that the argentous state (Ag (I), $\underline{d}^{10}$) is the normal and dominant oxidation state for silver may well account for this. Presumably, at the high temperature of the final stages of the thermal analysis, the AgF_2 disproportionates (e.g. $4AgF_2 \longrightarrow 2AgF + 2Ag + 3F_2$).

The details of the thermal decomposition of $SnF_2.AsF_5$ are shown in Figure 4. The first step in the disproportionation occurs rapidly in the temperature range 79 to $215^{\circ}C$ and 26.01% of the initial weight is lost which is close to that expected (25.9%) for the removal of half a mole of AsF_5. This step is accompanied by an endothermic DTA peak at $204^{\circ}C$. The second stage of the decomposition follows immediately and is finished at $275^{\circ}C$, the exothermic DTA peak and DTG minimum occurring at $252^{\circ}C$. [This extraordinary exothermic effect can only be reasonably accounted for in terms of partial oxidation of SnF_2 to SnF_4 (i.e. $2SnF_2.AsF_5 \longrightarrow SnF_2 + SnF_4 + AsF_3$) and subsequent decomposition of SnF_4 to SnF_2]. With increasing temperature further weight loss is slow but the weight becomes constant at $600^{\circ}C$. The observed total weight loss for the two steps of the decomposition is 49.2% which correlates well with that for loss of one mole of AsF_5 per mole of $SnF_2.AsF_5$.

EXPERIMENTAL

All the adducts were prepared by the methods outlined previously [1,2] and their purities were monitored by chemical analysis, vibrational spectroscopy and X-ray powder diffraction methods.

Chemical analysis for the samples for which a detailed thermal analysis is given are summarized below:

$PbF_2.2AsF_5$. Found: Pb,33.7; AsF_6^-, 62.2; Calc. :Pb,35.42; AsF_6^-, 64.58%.

$MnF_2.2AsF_5$. Found: Mn,12.7; AsF_6^-, 87.8; Calc. :Mn,12.69; AsF_6^-, 87.30%.

$2CuF_2.3AsF_5$. Found: Cu,17.3; AsF_6^-, 78.0; F_f^-, 2.3; Calc.: Cu, 17.83, AsF_6^-, 79.50; F_f^-, 2.67%.

$SnF_2 \cdot AsF_5$. Found: Sn,48.2; AsF_6^-, 38.7, F_f^-, 11.6; Calc.: Sn, 49.12, AsF_6^-, 39.09, F_f^-, 11.79%.

(F_f^- represents free fluoride which can be determined independently of fluorine bound to arsenic in AsF_6^- [11]).

A Mettler TA 1 Thermoanalyser was used for the thermal decomposition studies. In a typical run approximately 100 mg of sample was used and this was referenced against a 100mg sample of $\propto Al_2O_3$. The heating rate for the furnace was $6^{\circ}C$ min^{-1} and the decompositions were carried out in a dried argon atmosphere with a flow rate of 5 1 hr^{-1}. The DTG range was 5 mg hr^{-1} and the DTA range was 50 µV.

The gases given off in the thermal decompositions were characterized in static runs by infrared spectroscopy as pure arsenic pentafluoride. It is assumed that the products from the dynamic decompositions is the same.

ACKNOWLEDGEMENTS

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