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A STUDY OF AMMONIUM PLUTONIUM(IV) FLUORIDES – II

THE THERMAL DECOMPOSITION OF AMMONIUM PLUTONIUM(IV) FLUORIDES, AMMONIUM CERIUM(IV) FLUORIDE AND AMMONIUM URANIUM(IV) FLUORIDE

TANEAKI YAHATA, TADASUMI MUROMURA, KINJI OUCHI and KEIJI NAITO*
Chemistry Division, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan

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Abstract—Thermal decomposition of $PuF_4 \cdot 7/6NH_4F$ (or $PuF_4 \cdot NH_4F$), $PuF_4 \cdot 2NH_4F$, $CeF_4 \cdot 7/6NH_4F$ (or $CeF_4 \cdot NH_4F$) and $UF_4 \cdot 7/6NH_4F$ (or $UF_4 \cdot NH_4F$) have been studied under vacuum and in inert gas flow, using a microthermobalance. The anhydrous PuF_3, CeF_3 and UF_4 were obtained as the decomposition products. The following reactions appeared to occur in thermal decomposition of these double salts.

1 $MF_4 \cdot 7/6NH_4F = MF_3 + 5/6NH_4F + 8/6HF + 1/6N_2$ (M = Pu and Ce)
2 $UF_4 \cdot 7/6NH_4F = UF_4 + 7/6NH_4F$.

INTRODUCTION

MANY double salts are known between actinide elements and alkali fluorides. Among them, ammonium double fluorides are of special interest in the preparation of anhydrous fluorides, since the thermal decomposition of ammonium double salts yields the anhydrous fluorides which are to be used as the source materials for preparation of actinide metals.

Uranium tetrafluoride was prepared by thermal decomposition of ammonium uranium(IV) fluoride $UF_4 \cdot NH_4F$ which was obtained by wet method by Robinson [1] and also by Tolley[2].

Benz *et al.*[3] reported the formation of anhydrous double salts by the solid–solid reaction between PuF_4 and NH_4F and it was noted that the double salt decomposed to PuF_4 and a small fraction of which was consumed in a slow, unidentified side-reaction. Tolley[4] also reported the formation of ammonium plutonium(IV) fluoride by the reaction between plutonium dioxide and ammonium bifluoride, and the double salt decomposed to PuF_4 rapidly at 300°C,

$$PuF_4 \cdot NH_4F = PuF_4 + NH_4F.$$

The thermal decomposition of ammonium cerium(IV) fluoride obtained by dry method was reported by Asker *et al.*[5] as follows,

$$(NH_4)_2Ce_2F_9 = 2CeF_3 + 3HF + N_2 + 2\cdot5H_2.$$

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*Present address: Faculty of Engineering, Nagoya University Nagoya, Japan.

1. R. E. Robinson, J. C. Geertsma and J. C. Paynter, P/464 South Africa 264.
2. W. B. Tolley, HW-35814 (1955).
3. R. Benz, R. M. Douglass, F. K. Kruse and R. A. Penneman, *J. inorg. Chem.* **2**, 799 (1963).
4. W. J. Tolley, HW-31211 (1954).
5. W. J. Asker and A. W. Wylie, *Austral. J. Chem.* **18**, 959 (1965).

Although Penneman *et al.*[6] studied on the thermal decomposition of the several CeF_4–NH_4F double salts system by the thermogravimetric analysis and the differential thermal analysis, they made no mention of the formation of the anhydrous cerium fluoride as the decomposition products. Tolley[4] also reported that CeF_3 was formed by the thermal decomposition of ammonium cerium(IV) fluoride made by dry method, but they did not study the mechanism of the formation of CeF_3 instead of CeF_4.

In the present study, the thermal decomposition of some double salts, viz. $PuF_4 \cdot 7/6NH_4F$, $PuF_4 \cdot 2NH_4F$, $CeF_4 \cdot 7/6NH_4F$ and $UF_4 \cdot 7/6NH_4F$ prepared by the wet method[7] was investigated. The mechanism of the decomposition are discussed on the basis of thermodynamical data, comparing with the early results for double salts obtained by dry method.

EXPERIMENTAL

Preparation of the double salts

Ammonium plutonium(IV) fluorides. The procedure was described in the preceeding paper[7]. The pink colored double salt $PuF_4 \cdot 7/6\ NH_4F$ (or $PuF_4 \cdot NH_4F$) and the green colored double salt $PuF_4 \cdot 2NH_4F$ were used in the experiment.

Ammonium cerium(IV) fluoride. $Ce(SO_4)_2 \cdot 2H_2O$ was dissolved in water, to which 48% HF was added. A white precipitate formed and then disappeared with excess HF. The ammonium cerium(IV) fluoride was precipitated by addition of ammonium salt. Alternatively, $Ce(NO_3)_4 \cdot 2NH_4NO_3 \cdot 2H_2O$ was dissolved in water, 48% HF was then added to the solution until the precipitation was completed. The both precipitates obtained by the two methods showed the same X-ray patterns which are isostructural with that of $PuF_4 \cdot 7/6NH_4F$.

Ammonium uranium(IV) fluoride. Uranium metal was dissolved in HCl. A green precipitate was obtained by adding 5M NH_4F to the solution. This green colored double salt showed isostructural X-ray pattern with the pink ammonium plutonium(IV) fluoride and white ammonium cerium(IV) fluoride.

The double salts obtained in the above were washed with methanol and dried over $Mg(ClO_4)_2$.

Thermal decomposition of the double salts

From 10 to 50 mg of the double salt was placed on a platinum pan suspended in a microthermobalance (Cahn RG-type). The rate of heating was from 5 to 420°C per hr. Argon or helium as an inert gas had been purified by passing over hot copper and palladium asbestos and through liquid nitrogen.

RESULTS

Ammonium plutonium(IV) fluorides

The decomposition of $PuF_4 \cdot 2NH_4F$ was complete from 110 to 430°C; during the period, the color changed from green to pink and finally to violet.

$PuF_4 \cdot 7/6NH_4F$ (or $PuF_4 \cdot NH_4F$) decomposed gradually in the temperature range of 130°–430°C; the change in color was from pink to violet.

Figure 1 shows a thermal decomposition curve for $PuF_4 \cdot 7/6NH_4F$, where the stationary arrest of PuF_3 was attained by keeping at 250°C under vacuum. The stationary arrests corresponding the formation of $PuF_4 \cdot 1/3NH_4F$ and PuF_4 which are reported by Benz *et al.*[3] were not observed under the present experimental conditions. The final product violet in color was determined to be PuF_3 by X-ray diffraction.

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6. R. A. Penneman and A. Rosenzweig, *J. inorg. Chem.* **8**, 627 (1969).
7. T. Muromura, T. Yahata, K. Ouchi and K. Naito, *J. inorg. nucl. Chem.* **33**, (1971).

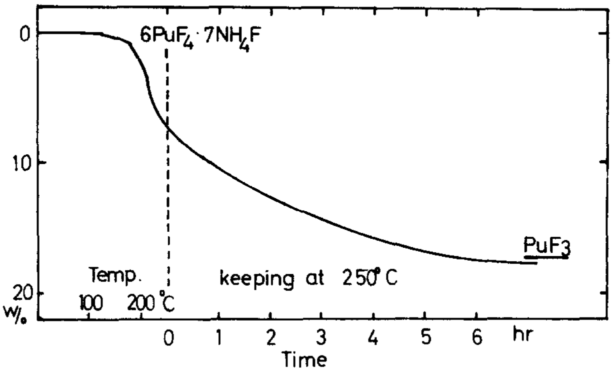

Fig. 1. Thermal decomposition of $PuF_4 \cdot 7/6NH_4F$. The run was made at the constant temperature indicated; after 7 hr, at 250°C.

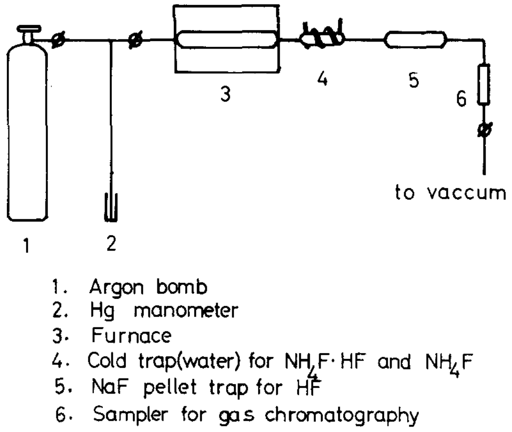

Fig. 2. Apparatus for collection of the evaporated materials.

Ammonium cerium(IV) fluoride

$CeF_4 \cdot 7/6NH_4F$ was decomposed in the temperature range of 130°–430°C in inert gas flow. The final product white in color was determined to be CeF_3 by X-ray diffraction; CeF_4 was not observed in the experiment.

The analysis of the evaporated materials was made by the apparatus shown in Fig. 2. The materials evaporated due to the thermal decomposition was confirmed to be $NH_4F \cdot HF$ and nitrogen, by means of chemical analysis, X-ray diffraction and gas chromatography.

Ammonium uranium(IV) fluoride

The thermal decomposition of $UF_4 \cdot 7/6NH_4F$ (or $UF_4 \cdot NH_4F$) is known well [1–3]. The final product in the present experiment was confirmed to be UF_4.

DISCUSSION

Although $PuF_4 \cdot 7/6\ NH_4F$ (or $PuF_4 \cdot NH_4F$), $CeF_4 \cdot 7/6NH_4F$ (or $CeF_4 \cdot NH_4F$) and $UF_4 \cdot 7/6NH_4F$ (or $UF_4 \cdot NH_4F$) showed the isostructural X-ray patterns, plutonium and cerium double salt yielded trifluoride as the thermal decomposition products, and uranium double salt yielded tetrafluoride.

The results for the decomposition products of cerium and uranium double salt obtained by wet method in this study were in agreement with those obtained by dry method by other workers[3–5]. As to the plutonium double salt, Benz *et al.*[3] reported that PuF_4 was formed the result of the thermal decomposition and it then suffered a side reaction which was not confirmed. Tolley[4] also obtained PuF_4, but the chemical analysis showed rather low fluorine content for the PuF_4; the mole ratio of fluorine to plutonium was from 3·2 to 3·9.

In the present experiment, however, PuF_3, instead of PuF_4, was obtained by thermal decomposition of the ammonium plutonium(IV) fluorides. The formation of PuF_3 as the decomposition products was explained by assuming the following reactions.

I. $MF_4\cdot 7/6NH_4F$ decomposes first to MF_4 and then to MF_3.

$$\begin{aligned} 1/6(6MF_4\cdot 7NH_4F) &= MF_4 + 7/6NH_4F \\ MF_4 &= MF_3 + 1/2F_2 \\ 1\ PuF_4 = PuF_3 + 1/2F_2 \qquad & \Delta G^\circ_{298} = 40\cdot 8\ \text{kcal/mole} \\ 2\ CeF_4 = CeF_3 + 1/2F_2 \qquad & \Delta G^\circ_{298} = 17\cdot 1\ \text{kcal/mole} \\ 3\ UF_4 = UF_3 + 1/2F_2 \qquad & \Delta G^\circ_{298} = 95\cdot 6\ \text{kcal/mole} \end{aligned} \tag{1}$$

These tetrafluorides are so stable that the reaction to the right would hardly occur at the experimental temperatures.

II. The reaction between PuF_4 and PuO_2 was suggested by Dawson[8] as follows:

$$3PuF_4 + PuO_2 = 4PuF_3 + O_2 \text{ (under vacuum at 600°C)} \tag{2}$$

In order to avoid the oxidation, ammonium plutonium(IV) fluoride was sealed in a quartz tube under vacuum with glittering uranium metal chips, then was decomposed at 230°C. Despite this prevention of the oxidation and low temperature reaction, the decomposition product was PuF_3. The Equation (2) therefore was not the case.

III. Finally the following reaction process was assumed. Ammonium fluoride decomposes to hydrofluoric acid and ammonia at high temperature, and the tetrafluoride is reduced to trifluoride in a ammonia atmosphere:

$$\begin{aligned} &1\ PuF_4 + 7/6NH_3 = PuF_3 + HF + 5/4H_2 + 7/12N_2\ \Delta G^\circ_{298} = -15\cdot 0\ \text{kcal/mole} \\ &2\ CeF_4 + 7/6NH_3 = CeF_3 + HF + 5/4H_2 + 7/12N_2\ \Delta G^\circ_{298} = -39\cdot 6\ \text{kcal/mole} \\ &3\ UF_4 + 7/6NH_3 = UF_3 + HF + 5/4H_2 + 7/12N_2\ \Delta G^\circ_{298} = +38\cdot 9\ \text{kcal/mole.} \end{aligned}$$

Table 1 shows the comparison for the standard free energy changes between the two probable reactions; the one yields tetrafluoride and the other trifluoride. As shown in Table 1, the double salts of plutonium(IV) and cerium(IV) were easily reduced to trifluoride but that of uranium(IV) was hardly reduced to trifluoride.

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8. J. K. Dawson, R. M. Elliott, R. Hurst and A. E. Truswell, *J. chem. Soc.* 558 (1954).

Table 1. Probable reactions and the free energy changes of the thermal decomposition of the double salts

$PuF_4{\cdot}7/6NH_4F = PuF_4 + 7/6NH_3 + 7/6HF$	$\Delta G^\circ_{298} = -482{\cdot}6$ kcal/mole
$PuF_4{\cdot}7/6NH_4F = PuF_3 + 13/6HF + 5/6NH_3 + 1/6N_2$	$\Delta G^\circ_{298} = -500{\cdot}6$ kcal/mole
$CeF_4{\cdot}7/6NH_4F = CeF_4 + 7/6NH_3 + 7/6HF$	$\Delta G^\circ_{298} = -499{\cdot}8$ kcal/mole
$CeF_4{\cdot}7/6NH_4F = CeF_3 + 13/6HF + 5/6NH_3 + 1/6N_2$	$\Delta G^\circ_{298} = -541{\cdot}8$ kcal/mole
$UF_4{\cdot}7/6NH_4F = UF_4 + 7/6NH_3 + 7/6HF$	$\Delta G^\circ_{298} = -500{\cdot}9$ kcal/mole
$UF_4{\cdot}7/6NH_4F = UF_4 + 13/6HF + 5/6NH_3 + 1/6N_2$	$\Delta G^\circ_{298} = -465{\cdot}0$ kcal/mole

The evaporated materials were confirmed to be $NH_4F{\cdot}HF$ by X-ray and chemical analysis, which is a recombined compound of ammonia with hydrofluoric acid. A large amount of nitrogen was also determined by using gas chromatography.

From the results of the decomposition products and evaporated materials, the following reactions were proposed:

$$MF_4{\cdot}7/6NH_4F = MF_3 + 5/6NH_4F + 8/6HF + 1/6N_2 \ (M = \text{Pu and Ce}) \quad (3)$$

$$UF_4{\cdot}7/6NH_4F = UF_4 + 7/6NH_4F. \quad (4)$$

Plutonium and cerium tetrafluoride may be obtained from the thermal decomposition of ammonium double fluoride under oxidative atmosphere but it will be easily oxidized by moisture, so that it is difficult to obtain PuF_4 and CeF_4 in pure forms.

Tolley[4], as mentioned above, reported the production of PuF_4 by thermal decomposition of ammonium plutonium(IV) fluoride. The product of "tetrafluoride" obtained in their study, however, was rather low content of fluorine and X-ray patterns of the "tetrafluoride" were not given. Benz *et al.*[3] reported the formation of pink fine crystal of PuF_4 which was confirmed by observing X-ray pattern. Although it is not clear why the plutonium tetrafluoride was formed in their experiment, it might be obtained during thermal decomposition in dry oxidative atmosphere.

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