ACTA CHEMICA SCANDINAVICA 19 (1965) 2136–2138

The Thermal Decomposition of NbO_2F

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The decomposition of NbO_2F in an argon atmosphere to α-Nb_2O_5 has been found to pass through Nb_3O_7F and the N-form of Nb_2O_5. The decomposition occurs by the formation of the gas molecule $NbOF_3$ and the losses of weight observed are in agreement with the following decomposition formulae:

$$4\ NbO_2F(s) = Nb_3O_7F(s) + NbOF_3(g)$$
$$3\ Nb_3O_7F(s) = 4\ Nb_2O_5(s) + NbOF_3(g)$$

The phase analysis of the system NbO_2F—Nb_2O_5, performed in sealed platinum capsules at temperatures between 500°C—1100°C, revealed the following four compounds: Nb_3O_7F, $Nb_5O_{12}F$, $Nb_{17}O_{42}F$, and $Nb_{31}O_{77}F$.[1-3] In order to learn whether these phases could be synthesized by a different technique, studies on the thermal decomposition of NbO_2F were taken up.

EXPERIMENTAL

NbO_2F was synthesized by dissolving Nb_2O_5 (Kawecki, 99.99 %) in aqueous hydrogen fluoride and the clear solution was then evaporated to dryness. The product was heated in a stream of dried argon at 400°C for a few hours. NbO_2F was then identified by means of its Guinier powder pattern.[1] The thermal decomposition of NbO_2F was performed by heating a sample of NbO_2F in a slow stream of dried argon in a horizontal furnace. The sample, kept in a platinum boat, was heated stepwise up to 1320°C. For every observation, marked with a circle in Fig. 1, the sample was kept at the temperature for 10 min and then weighed at room temperature. In a separate run, nine samples were taken out at different temperatures, indicated by arrows in Fig. 1, in order to obtain X-ray powder pattern identification of the phase present.

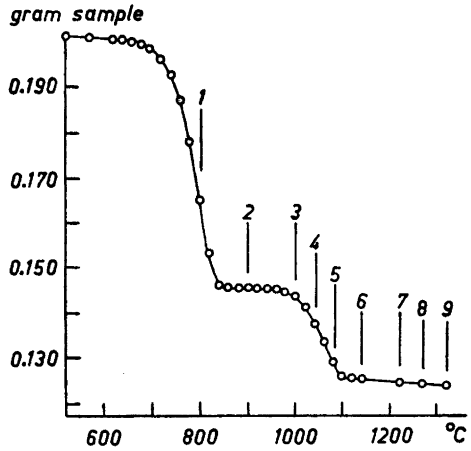

Fig. 1. The thermal decomposition of NbO_2F.

RESULTS OF THE THERMAL DECOMPOSITION AND DISCUSSION

The decomposition curve is given in Fig. 1. Table 1 shows the X-ray powder identification of the phases formed. The plateau at temperatures between 840°C and 970°C corresponds to pure Nb_3O_7F. Large amounts of the compound can thus be made in this way. Although a small loss of weight was observed between 1100°C and 1270°C, the X-ray powder patterns showed only one phase, *viz.* the N-Nb_2O_5. At 1320°C the powder pattern showed only the high temperature form of niobia, α-Nb_2O_5.

The total losses of weight for two separate runs were 38.2 and 37.2 %, respectively. If the overall reaction

$$3\ NbO_2F(s) = Nb_2O_5(s) + NbOF_3(g)$$

is assumed, the calculated loss of weight is 38.4 %. For the reaction

$$5\ NbO_2F(s) = NbF_5(g) + 2\ Nb_2O_5(s)$$

Table 1. X-Ray powder analysis of samples from the thermal decomposition of NbO_2F according to Fig. 1.

Sample	Phases present
1	NbO_2F + Nb_3O_7F
2	Nb_3O_7F
3	Nb_3O_7F + small amount of N-Nb_2O_5
4	Nb_3O_7F + increasing amount of N-Nb_2O_5
5	small amount of Nb_3O_7F + N-Nb_2O_5
6	N-Nb_2O_5
7	N-Nb_2O_5
8	N-Nb_2O_5 + α-Nb_2O_5
9	α-Nb_2O_5

the calculated loss of weight is 26.1 %. The experimentally observed losses of weight thus agree very well with the assumption that $NbOF_3$ is formed.

For the first step,

$$4\ NbO_2F(s) = Nb_3O_7F(s) + NbOF_3(g)$$

the two observed losses of weight, 28.5 and 28.2 %, respectively, agree very well with the one calculated, *viz.* 28.8 %.

The existence of the gaseous molecule $NbOF_3$ has been predicted by Schäfer.[4] N-Nb_2O_5 was first synthesized by Schäfer *et al.*[5] with the transport reaction

$$Nb_2O_5(s) + 3\ NbCl_5(g) = 5\ NbOCl_3(g)$$

N-Nb_2O_5 has also been obtained under hydrothermal conditions.[6] The N-Nb_2O_5 formed during this thermal decomposition seems to have a small amount of fluorine incorporated in its lattice. This can very well be understood from its crystal structure and will be discussed separately.[6]

REFERENCES

1. Andersson, S. and Åström, A. *Acta Chem. Scand.* **18** (1964) 2233.
2. Andersson, S. *Acta Chem. Scand.* **18** (1964) 2339.
3. Andersson, S. *Acta Chem. Scand.* **19** (1965) 1401.
4. Schäfer, H. *Chemische Transportreaktionen*, Verlag Chemie, Weinheim 1962.
5. Schäfer, H., Schulte, F. and Gruehn, R. *Angew. Chem.* **76** (1964) 536.
6. Andersson, S. *Unpublished results.*

Received July 20, 1965.