Journal of Thermal Analysis Vol. 33 (1988) 811–815

A COMPARISON OF THE THERMAL BEHAVIOUR OF α-AlF$_3$ AND ALUMINIUM FLUORIDE HYDRATES

D.-H. Menz, A. Zacharias and *L. Kolditz*

CENTRAL INSTITUTE OF INORGANIC CHEMISTRY OF THE ACADEMY
OF SCIENCES OF THE G.D.R., 1199 BERLIN, G.D.R.

The thermal decompositions of β-AlF$_3\cdot 3H_2O$, AlF$_3\cdot 3.5H_2O$, AlF$_3\cdot 1.5H_2O$, β-AlF$_3$ and hydroxyfluorides of aluminium were investigated. The literature data were complemented with X-ray results. The first stages of decomposition are described. The AlF$_3$ hydrates and hydroxyfluorides were used as model systems in order to interpret the thermal behaviour of α-AlF$_3$ in more detail.

A mass-spectrometric study showed the very complicated nature of hydrolysis processes occurring during the interaction of water traces and α-AlF$_3$ [1]. Pure α-AlF$_3$ loses its water traces up to 600°. As a result of the hydrolysis, not only HF, but also gaseous HF–AlF$_3$ complexes are formed. The formation of these complexes depends strongly on the temperature, and it is possible to subdivide the process of hydrolysis into 3 temperature-dependent ranges. The first step (up to 250°) is characterized by water loss and the continuous formation of HF. In the second temperature range (250–550°), the first maximum, due to the formation of HAlF$_4$, can be observed. The temperature range above 600° is also characterized by the formation of gaseous complexes, but the species are not the same. Only one phase transition in α-AlF$_3$ is known, at $452 \pm 10°$, but it is impossible to correlate the formation of gaseous complexes with this transition. During the preparation of α-AlF$_3$, traces of hydrates of AlF$_3$ or hydroxyfluorides of Al can be formed. These compounds are a source of water and they modify the thermal behaviour of AlF$_3$. A large number of papers have reported on several hydrates of aluminiumfluoride and hydroxyfluorides of Al (see, for example, Grobelny [2]), but the results are not consistent in all cases. Accordingly, it was necessary to reinvestigate several compounds under the same conditions. On the basis of the literature data, we selected β-AlF$_3\cdot 3H_2O$, AlF$_3\cdot 3.5H_2O$, AlF$_3\cdot 1.5H_2O$, β-AlF$_3$ and hydroxyfluorides. These compounds show thermal effects in the temperature range of interest.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

Table 1 details the preparation methods and the results of chemical analysis of the compounds used. Fluorine was determined according to Seel [3] and aluminium with EDTA. The thermal analysis was carried out with a Q 1500 D derivatograph. Experimental conditions: Pt crucibles, sample mass 200–400 mg, α-Al_2O_3 as reference substance, heating rate 3 deg min^{-1} (Q) and 5 deg min^{-1} (dynamic), rate of decomposition 2 mg min^{-1}. X-ray powder diffraction patterns were obtained with a Guinier camera with a heating device (heating rate 2.5 deg min^{-1}, 20–900°, flowing N_2). The conditions for the determination of the gaseous complex species are given in [1].

Table 1 Results of chemical analysis

Compound	Chemical analysis		Preparation according to
	Al, m% (th)	F, m% (th)	
β-$AlF_3 \cdot 3H_2O$	19.1 (19.55)	40.3 (41.3)	[5]
$AlF_3 \cdot 3.5H_2O$	18.1 (18.45)	38.9 (38.75)	[5]
$AlF_3 \cdot 1.5H_2O$	23.9 (24.3)	57.1 (51.4)	[7]
	24.1 (24.3)	55.3 (51.4)	evaporation of HF acidic AlF_3 solution to dryness
β-AlF_3	35.4 (32.1)	64.1 (67.9)	[6]
γ-AlF_3	32.1 (32.1)	67.9 (67.9)	[6]

Results and discussion

The release of H_2O traces from pure α-AlF_3 was observed in the temperature range from 80 to 600°, with a maximum at 210°. This is in good agreement with the temperature range of the dehydration of β-$AlF_3 \cdot 3H_2O$ and $AlF_3 \cdot 3.5H_2O$, described by Petzold et al. [4] and Schmidt [5]. If complete dehydration takes place, both compounds undergo a hydrolysis process. However, the mechanisms of hydrolysis are not the same. β-$AlF_3 \cdot 3H_2O$ is more stable then $AlF_3 \cdot 3.5H_2O$. The X-ray powder patterns of the reaction products show that the decompositions are more complicated than described in the literature. Only heating over a long time (2–4 h) leads to well-known decomposition products, especially γ-AlF_3 [6] and β-AlF_3. The first reaction steps were determined in short-time experiments. The results are given in Table 2. High-temperature X-ray investigations did not show significant differences between β-$AlF_3 \cdot 3H_2O$ and $AlF_3 \cdot 3.5H_2O$. Above 125°, the X-ray photograph reveals no diffraction lines, which means that the products of

Table 2 Results of X-ray investigation

Compound	Decomposition products after heating (15 min)			
	100 °C	200 °C	300 °C	400 °C
β-$AlF_3 \cdot 3H_2O$	β-$AlF_3 \cdot 3H_2O$	amorphous	γ-AlF_3 [6] traces of β-AlF_3	γ-AlF_3 [6] traces of β-AlF_3
$AlF_3 \cdot 3.5H_2O$	$AlF_3 \cdot 3.5H_2O$	amorphous	γ-AlF_3 [9]	β-AlF_3
$AlF_3 \cdot 1.5H_2O$	$AlF_3 \cdot 1.5H_2O$	$AlF_3 \cdot 0.5H_2O$	ε_3-AlF_3 [7] γ-AlF_3 [9]	γ-AlF_3 [9]

decomposition are amorphous. At temperatures above 320°, crystalline β-AlF_3 occurs. At 625°, the transition of β-AlF_3 into the high-temperature modification of α-AlF_3 takes place, accompanied by hydrolysis. As concerns these features, one must interpret the heating process of AlF_3 in more detail. In order to explain the evaporation effect of AlF_3 at 360°, it is helpful to investigate the thermal behaviour of hydroxyfluorides of Al and $AlF_3 \cdot 1.5H_2O$ (ε_1-AlF_3 [7]). The formula $AlF_3 \cdot 1.5H_2O$ is only an idealized one. The composition of this compound varied with the conditions of preparation. There are two possibilities for the preparation of this compound, which is characterized by the powder patterns as in [7]. Vacuum evaporation of a solution of AlF_3 leads to poorly crystallized compounds, Better-crystallized products were obtained by evaporation of an acidic solution (HF) to dryness. However, the F contents of the products are too high in both cases. Details on the thermal behaviour of "$AlF_3 \cdot 1.5H_2O$" have not yet been published. Our thermal and X-ray analysis results are given in Table 2 and Fig. 1. After the main step at 200° in the TG curves, the further mass loss proceeds continuously, similarly as when the Q-technique is used. It should be noted that the mass loss caused is not

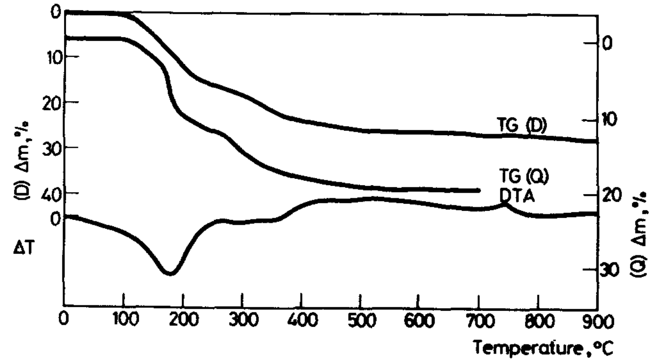

Fig. 1 Thermal analysis of $AlF_3 \cdot 1.5H_2O$, powder patterns according to [7] (400 mg, 5 K min^{-1})

only by dehydration, but also by hydrolysis. The thermal effect at 746° depends on the F content. At higher F content, it is shifted to lower temperature (630°). In the process of decomposition of $AlF_3 \cdot 1.5H_2O$, no crystalline hydroxyfluorides are formed. However, it may be assumed that amorphous species of this composition play an important role in this decomposition process. The main step in the decomposition proceeds at the same temperature as the formation of $HAlF_4$. The formation of the complexes in the temperature range above 600° can be interpreted in terms of the decomposition of special forms of hydroxyfluorides.

Grobelny [2] described a phase transition of β-AlF_3 at 640°. High-temperature X-ray investigations show that this transition is connected with hydrolysis. As a result of the hydrolysis, the diffraction lines in the X-ray photograph vanish. To summarize the different effects, such as those of the preparation conditions, the results of chemical analysis and the pathway of decomposition lead us to suppose that β-AlF_3 is a variety of γ-AlF_3, agreeing with [9], stabilized by hydroxyl ions. Therefore, it is reasonable to define the thermal effect at 640° as a decomposition point.

Bulgakov [10] reported exothermic effects above 700°, due to the solid-state reaction between AlF_3 and Al_2O_3.

We have found that reaction takes place only if the Al_2O_3 contains hydroxyl ions. When α-Al_2O_3 was used, no thermal effects were observed. The thermal effects were split if a product with an AlF_3 content lower than 96% was used. The splitting is caused by several processes. Above 800°, a mineralization process must be considered, and below 600°, decomposition of the hydroxyfluoride species takes place. This comparison of the thermal behaviour of AlF_3, AlF_3 hydrates and hydroxyfluorides confirmed that it is possible to explain the thermal effects occurring during the heating of α-AlF_3 on the basis of the properties of AlF_3 hydrates and hydroxyfluorides.

References

1 D.-H. Menz, L. Kolditz, K. Heide, C. Schmidt, Ch. Kunert, Ch. Mensing, H. G. v. Schnering and W. Hönle, Z. Anorg. Allgem. Chem., prepared for press.

2 M. Grobelny, J. FLuozine Chem., 9 (1977) 187.

3 F. Seel, E. Steigner and I. Burger, Angew. Chem., 76 (1964) 532.

4 D. Petzold, W. Matthes and R. Naumann, Wiss. Beiträge d. Friedrich-Schiller-Universität Jena 1961, p. 22.

5 A. Schmidt, Monats. Chemie, 98 (1967) 482.

6 F. J. Christoph and G. Teufer, US Pat. 3 178 484/1965 and 3 178 483/1965.

7 H. Wada, Y. Kawakami and T. Kamihigoshi, US Pat. Nr. 3 929 415/1975.

8 P. A. Foster, J. Elektrochem. Soc., 106 (1959) 971.

9 D. B. Shinn, D. S. Crocket and H. M. Haendler, J. Inorg. Chem., 5 (1966) 1927.

10 O. V. Bulgakov and T. V. Antipina, Zh. Fiz. Khim., 42 (1968) 2060.

Zusammenfassung — Die thermische Zersetzung von β-$AlF_3 \cdot 3H_2O$, $AlF_3 \cdot 3{,}5H_2O$, $AlF_3 \cdot 1{,}5H_2O$, β-AlF_3 und Hydroxyfluoriden des Aluminiums wurden untersucht und die in der Literatur beschriebenen Ergebnisse durch Röntgenuntersuchungen ergänzt. Die ersten Phasen der Zersetzung werden beschrieben. Die AlF_3-Hydrate und Hydroxyfluoride des Aluminiums können als Modellsystem genutzt werden, um das thermische Verhalten von α-AlF_3 detailliert zu beschreiben.

Резюме — Изучено термическое разложение β-$AlF_3 \cdot 3H_2O$, $AlF_3 \cdot 3{,}5H_2O$, $AlF_3 \cdot 1{,}5H_2O$, β-AlF_3 и оксифторидов алюминия. Литературные данные были дополнены данными рентгенофазового анализа. Описаны первые стадии разложения этих соединений. Гидраты фторида алюминия и оксифториды алюминия были использованы в качестве модельных соединений для детальной интерпретации термического поведения α-AlF_3.