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ON THE REDUCTION OF Cr^{3+} DURING THE THERMAL DECOMPOSITION OF FLUOROCHROMATES(III) WITH NITROGEN CONTAINING CATIONS

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Abstract

The thermal decomposition of $[CO(NH_2)_2H]CrF_6{\cdot}H_2O$, $(C_3N_6H_8)CrF_5{\cdot}H_2O$ and the solid state reaction of CrF_3 and melamine are investigated under non-reciprocal quasi-static conditions and compared with the thermal behaviour of other fluorochromates(III) ($[Cr(NH_3)_6]CrF_6$, $(NH_4)_3CrF$ and $[C(NH_2)_3]_3CrF_6$). The comparison of the results shows that the amount of chromium(II) in the final product is determined by the thermal stability and consequently by the decomposition temperature of the intermediates. Neither bonding properties in the starting materials nor the absolute amount of generated NH_3 influence the composition of the final product.

Keywords: $(C_3N_6H_8)CrF_5{\cdot}H_2O$, $[C(NH_2)_3]_3CrF_6$, $[CO(NH_2)_2H]CrF_6{\cdot}H_2O$, $[Cr(NH_3)_6]CrF_6$, $(NH_4)_3CrF_6$, quasi-static thermal analysis, reduction of fluorochromates(III)

Introduction

Several processes participate in the thermal decomposition of fluorometallates with nitrogen containing cations, namely thermal dissociation, hydrolysis reactions, and pyrolysis of the cations. These partial reactions are influenced differently by changes in the partial pressure of the gaseous reaction products, and therefore these partial pressures strongly influence the whole decomposition process [1].

Using quasi-static thermoanalytical methods, the thermal decomposition occurs under conditions of quasi equilibrium, and the degree of hydrolysis can be

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estimated with the help of the Tschebull-Kepplinger equation [1, 2]. The products from the reduction reactions can be estimated with the help of oxidation state diagrams [3].

According to earlier experiences [3] one can expect formation of chromium(II)-fluoride during the decomposition of fluorochromates with nitrogen containing cations, as NH_3 is always an important component of the gaseous reaction products. However, only for the decomposition of guanidinium hexafluorochromate there is an agreement between experimental and predicted results. In the case of hexammine-chromium hexafluorochromate no reduction takes place and pure rhombohedral CrF_3 is formed [4]. Rhombohedral CrF_3 is also the main product from the thermal decomposition of $(NH_4)_3CrF_6$, only traces of Cr_2F_5 are detectable [5].

In order to clarify and explain these differences, three other thermal decomposition reactions were investigated under controlled atmosphere and compared with the results given above. The three reactions are the thermal decomposition of urea hexafluorochromate monohydrate and melammonium pentafluorochromate monohydrate and the solid state reaction of melamine and CrF_3. NH_3 is generated either by condensation or by pyrolysis reactions of the investigated compounds at elevated temperatures. In order to decide the influence of decomposition temperature and generated amount of NH_3 on the results of the decomposition reactions, the compared compounds and reactions were selected in such a way that these parameters varied within a wide range.

Experimental

The thermal analysis was carried out with the Derivatograph Q1500D which was modified for analysing highly reactive substances [5] and coupled with a MC80 computer. Non-reciprocal quasi-isobaric conditions were obtained using a Q-crucible [1] in which the partial pressure of the gaseous reaction products reaches 70 kPa (self-generated atmosphere). The following parameters were used: sample mass: 200–400 mg; dynamic heating rate: 5 deg·min^{-1}; atmosphere: N_2; pumping: 8 l/h; reference: Al_2O_3; crucible material: Pt.

Preparation of the investigated compounds

Urea hexafluorochromate monohydrate: $[CO(NH_2)_2H]_3CrF_6 \cdot H_2O$ crystallized from a solution of chromium metal and an aliquote solution of urea in 40% HF. Analytical results: M 367.2; N 24.26 (calc. 22.89)%; Cr 14.12 (14.16)%; F 30.4 (31.05)%.

Melammonium pentafluorochromate monohydrate: $(C_3N_6H_8)CrF_5 \cdot H_2O$ crystallized from a solution of chromium(III)fluoride in 40% HF after adding aliquote amount of melamine solved in 40% HF. Analytical results: M 293.16; N 29.26 (calc. 28.67)%; Cr 16.98 (17.74)%; F 33.17 (32.41)%.

The preparation and characterization of the other samples is described elsewhere [3–5]. The characterization of intermediates and of the final products of the decomposition was performed by X-ray analysis (Guinier-method, CuKα-radiation) and by i.r. spectroscopy (Specord, KBr-tablets) after cooling to room temperature.

Results

Figure 1 shows the results of thermal analysis of urea hexafluorochromate monohydrate under non-reciprocal quasi-isobaric conditions (70 kPa). The decomposition process begins at 150°C, and the mass loss of the first decomposition step agrees with the liberation of 1 mol water and 1 mol CO_2. Further decomposition in the temperature range of 150 to 490°C is accompanied by the formation of NH_3 and CO_2. At 500°C the hexagonal tungsten bronze type form of CrF_3(HTB-CrF_3) [6] was detected as the first crystalline decomposition product in the residue. This compound is formed once again via $CrF_3{\cdot}xNH_3$ (x ca. 1), which has been characterized by i.r. spectroscopy and described elsewhere [5]. The transformation of HTB-CrF_3 into the rhombohedral modification at 630°C is linked to a partial reduction of CrF_3. It should be noted that –

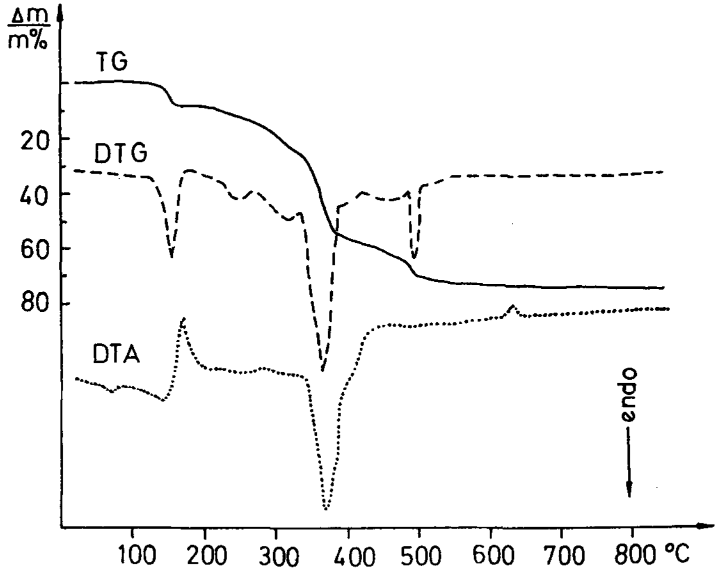

Fig. 1 Thermal analysis of urea hexafluorochromate monohydrate under non-reciprocal quasi-isobaric conditions

in correspondence with the findings in [5] – the partial reduction of CrF_3 during the phase transformation takes place simultaneously with a mass loss and an exothermic effect.

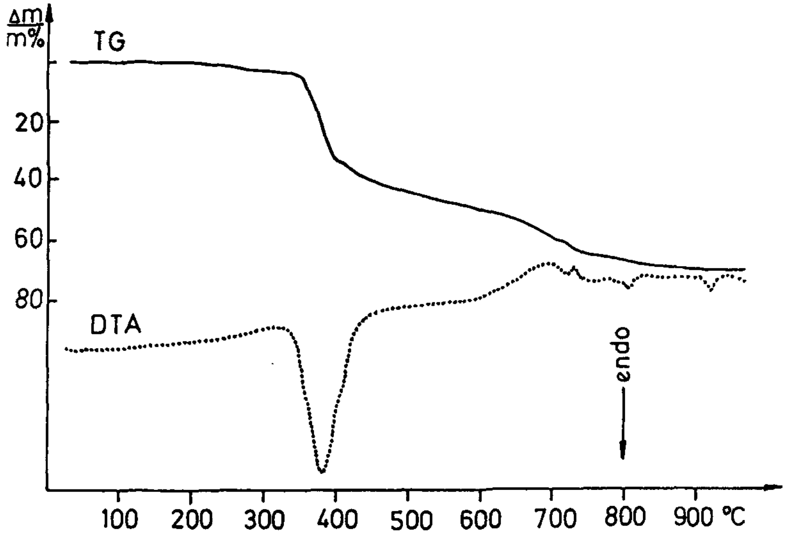

Fig. 2 Thermal analysis of guanidinium hexafluorochromate under non-reciprocal quasi-isobaric conditions

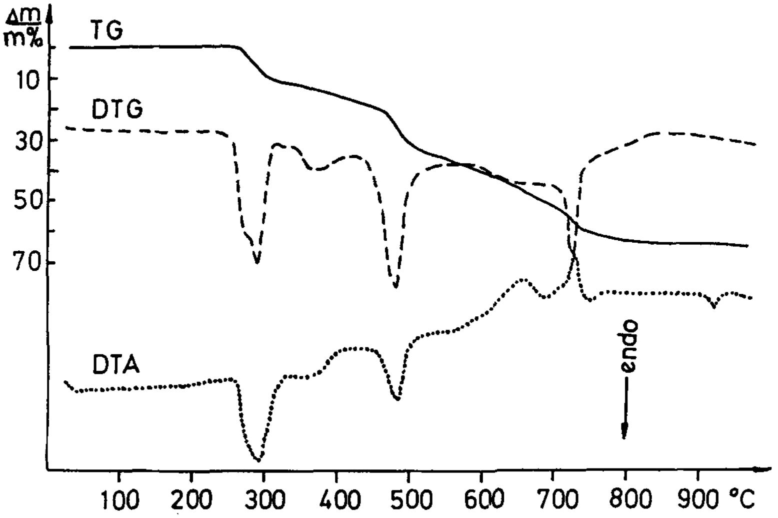

Fig. 3 Thermal analysis of melammonium pentafluorochromate monohydrate under non-reciprocal quasi-isobaric conditions

Figures 2–4 allow the comparison of the thermal decomposition of guanidinium hexafluorochromate with the thermal decomposition of melammonium pentafluorochromate monohydrate and the solid state reaction of CrF_3 with melamine. The initial steps of the decomposition reactions – up to 600°C – are complicated and consist of dehydration reactions (melammonium pentafluorochromate monohydrate) and several different decomposition processes of nitrogenous cations (see e.g. [7]). The final thermogravimetric step in all these three examples occurs at higher temperatures (about 700°C) than for other fluorochromates. The reason for this is that the nitrogenous cations undergo condensation reactions which lead to the formation of amorphous intermediates of high thermal stability. As illustrated in Fig. 5 other C–N bonds as in the starting materials are formed during these processes. The vibration at 2000 cm^{-1} in the i.r. spectrum of the solid residue of the thermal decomposition of guanidinium hexafluorochromate at 710°C is assigned to a Cr≡N bond. $CrF_3 \cdot xNH_3$ was not identified as an intermediate in these cases.

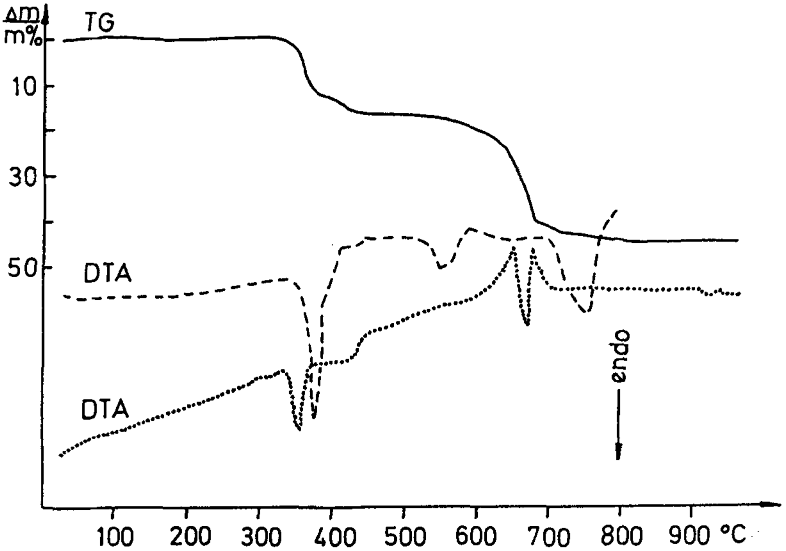

Fig. 4 Thermal analysis of the solid state reaction of CrF_3 and melamine under non-reciprocal quasi-isobaric conditions
— TG
···· DTA > of the reaction
--- DTA melamine

A common feature of the thermal decomposition of guanidinium hexafluorochromate, melammonium pentafluorochromate monohydrate and the solid state reaction of CrF_3 with melamine is an exothermic process which overlays the last (endothermic) mass loss. We interprete this effect as due to the main reduc-

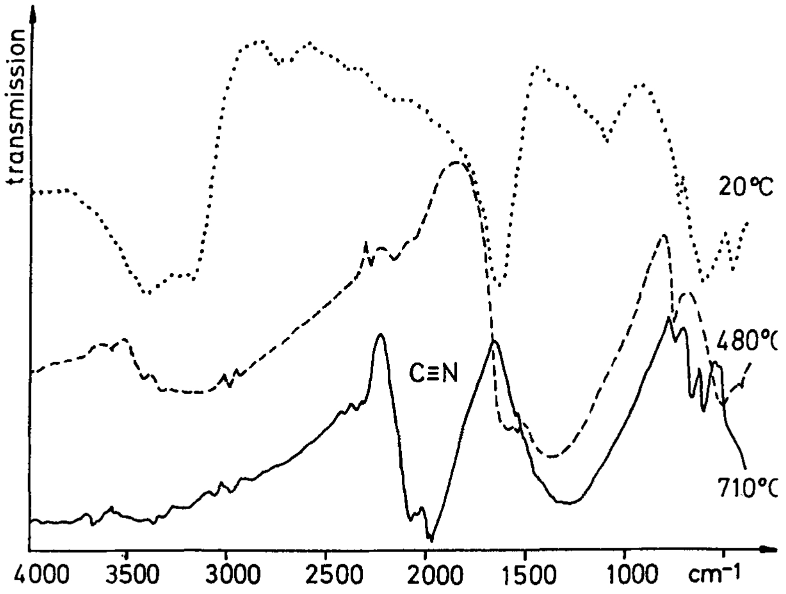

Fig. 5 I.r. spectra of intermediates and products of the thermal decomposition of guanidinium hexafluorochromate

tion reaction during the whole decomposition process. This reaction step leads to the final products during thermal decomposition of the guanidinium hexafluorochromate (CrF_2, CrN) and during solid state reaction of CrF_3 and melamine (Cr_2F_5). In the case of the decomposition of melammonium pentafluorochromate monohydrate β-CrN is formed as an intermediate. β-CrN is completely and irreversibly transformed into a mixture of CrN and CrF_2 when heated above 920°C.

Discussion

Decomposition temperatures and product compositions, as determined by X-ray powder diffraction, are given in Table 1. Comparison of the results shows an increasing amount of Cr^{2+} in the final product with an increasing temperature of decomposition. The expected formation of CrF_2 [3] is only observed when the final step of the decomposition of the fluorochromates proceeds at temperatures above 700°C. If the final step proceeds below this temperature, reduction only happens if the transformation of the intermediate HTB-CrF_3 into rhombohedral CrF_3 is exothermic and the transformation appears simultaneously with a mass loss.

The final products are determined by the structure and the thermal stability of the intermediates, and are neither influenced by the nature of the Cr–N bonds in the starting material nor by the absolute amount of NH_3 generation ([4] and [5]).

Reduction of Cr^{3+} does not only occur by interaction with gaseous NH_3 or amines, both generated during the decomposition. It may also be due to solid state reactions in the residue, like reaction with pyrolytically formed carbon. The significance of the latter reduction process increases with the amount of carbon in the cations.

Table 1 Decomposition products of fluorochromates with different nitrogenous cations (partial pressure of gaseous reaction products >70 kPa)

Compound	Max. temp. of NH_3 generation °C ($T_{max.}$ DTA)	Crystalline products	Ref.
$[Cr(NH_3)_6]CrF_6$	560 (rhomb. CrF_3 without any caloric effect)	CrF_3	4
$(NH_4)_3CrF_6$	530 (formation of CrF_3 at 620°C with Δm)	CrF_3, traces of Cr_2F_5	5
$[CO(NH_2)_2H]_3CrF_6 \cdot H_2O$	630	CrF_3, Cr_2F_5	*
CrF_3 + melamine	685	Cr_2F_5	*
$[C_3N_6H_8]CrF_5 \cdot H_2O$	724	CrF_2, CrN	*
$[C(NH_2)_3]_3CrF_6$	750	CrF_2, CrN	*

* this paper

As seen in Table 1, the thermal decomposition of melammonium and guanidinium fluorochromates on one side and the solid state reaction between CrF_3 and melamine on the other side lead to different final products. There are two reasons for this behaviour. Firstly, the thermal stability of melamine decreases by addition of CrF_3 (decomposition temperature decreases from 380 to 360°C; Fig. 4). The temperature of the final mass loss caused by decomposition of nitrogenous compounds is then too low for a total reduction of CrF_3. Secondly, the interaction between the thermolysis products of the nitrogenous compound and the fluoride is much more efficient in the case of a decomposition of a fluorochromate than in the case of a solid state reaction of a mechanical mixture of the two reagents.

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Zusammenfassung — Die Reduktion von Cr^{3+} ist eine der wesentlichsten Nebenreaktionen bei der thermischen Zersetzung von Fluorochromaten(III) mit stickstoffhaltigen Kationen. Die thermische Zersetzung von Ureahexafluorochromatmonohydrat, Melammoniumpentafluorochromatmononohydrat und die Festkörperreaktion zwischen CrF_3 und Melamin wurde unter nicht-reziproken quasi-isobaren Bedingungen untersucht und mit dem thermischen Verhalten weiterer Fluorochromate(III) verglichen. Der Vergleich der Ergebnisse zeigt, daß der Anteil von Chromium(II) im Endprodukt bestimmt wird durch die thermische Stabilität und damit durch die Zersetzungstemperatur der Zwischenprodukte, nicht aber durch die Bindungsverhältnisse in den Strukturen der Ausgangsverbindung und auch nicht durch die absolute Menge an generierten NH_3.