ELECTRONEGATIVITY FORCE OF CATIONS AND THERMAL DECOMPOSITION OF COMPLEX FLUORIDES

II. Thermal decomposition of fluoroborates

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Abstract

The thermal decomposition of anhydrous fluoroborates MBF$_4$ (M=Li, Na, K, Rb, Cs) and M(BF$_4$)$_2$ (M=Ca, Sr, Ba) was investigated. The decomposition proceeds according to a simple acid-base mechanism with evolution of BF$_3$. The influence of the acidity of cationic counter-ions, expressed by the electronegativity force on the course of thermal decomposition was estimated quantitatively.

Keywords: complexes, electronegativity, fluoroborates

Introduction

A large number of data are available in the chemical literature on the thermal decomposition of fluoroborates [1–6]. We have not found, however, any paper containing a broad spectrum of salts with various cationic counter-ions, differing largely in their acidic properties.

The decomposition of fluoroborates, like the decomposition of fluorosilicates presented in the 1st part of this paper [7], proceed with no participation of redox reactions. Hence it may appear suitable for verifying the idea that the electronegativity force [8] is a parameter which can be used for the quantitative description of the acidic properties of cations.

In the first part of this paper, devoted to the description of fluorosilicates, we have shown that a linear correlation exists between the electronegativity force and the reciprocal of the temperature of maximum rate of mass loss, due to the evolution of SiF$_4$, determined by thermal analysis. The electronegativity force has been defined as the ratio of ionization energy required to obtain the given cation to its ionic radius. It is known that the ionic radius depends on the coor-
dination number of the cation and on the sort of ligands involved. A list of values of electronegativity force calculated for cations with fluoride ligands has been given in part I of this paper.

It is to be pointed out that the above definition of electronegativity force cannot be used for characterizing hydrated cations, since in such cases the interaction with ligands (e.g. F⁻) is weaker than in the case of non-hydrated cations. For this reason we have studied the decomposition of anhydrous salts.

The aim of this study was to determine the course and the temperature of thermal decomposition of anhydrous fluoroborates, and to correlate the results obtained with the calculated electronegativity forces of the cations. The studies were based on thermal analysis, and X-ray phase analysis as well as infrared spectroscopy were used in the analysis of the starting materials and products of decomposition.

**Experimental**

Thermal analyses were performed using a derivatograph produced by MOM Budapest. Samples of salts (about 0.15 g) were put in platinum crucibles and placed in a quartz envelope with constant flow of purified nitrogen. The standard rate of heating was 9 deg.min⁻¹. The T, TG, DTG and DTA curves were recorded. X-ray analysis were performed by means of the powder method using a bicircular diffractometer TUR-M62 and CuKα radiation. As X-ray standards we used the values published by the Joint Committee on Powder Diffraction Standards or those found in other papers [9]. The infrared spectra of samples in KBr tablets were recorded by a SPECORD 75IR spectrophotometer in the range of 2000–400 cm⁻¹.

Potassium, rubidium, and caesium fluoroborates were precipitated as anhydrous salts by the action of 40% aq. HBF₄ (anal. grade, POCH) on aqueous solutions of KOH, Rb₂CO₃ and Cs₂CO₃, respectively. Lithium, barium, strontium, and calcium fluoroborates were crystallised from aqueous solutions obtained in reactions of the corresponding hydroxides (nitrite in case of barium) or carbonates with 40% aq. HBF₄. After separation of the precipitated fluorides the solutions were concentrated by evaporation under vacuum in the presence of silica gel. The crystals formed were dried under vacuum in the presence of P₂O₅ at a temperature of 40–50°C. NaBF₄ was crystallized from a solution obtained in the neutralization of NaOH by means of 40% aq. HBF₄ and concentrated under vacuum. Powder diffraction patterns of the anhydrous salts were in accord with ASTM standards: NaBF₄ 11-571, RbBF₄ 18-1131, CsBF₄ 9-394, Ca(BF₄)₂ 14-508, Sr(BF₄)₂ 14-509, Ba(BF₄)₂ 19-138. We had no LiBF₄ standard available, and the KBF₄ diffraction patterns was in accord with literature data [9].

The products of thermal decomposition were identified by X-ray diffraction in samples obtained on heating the corresponding salts in a tubular furnace in