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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-

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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 CuK$_\alpha$ 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. HBF_4 (anal. grade, POCH) on aqueous solutions of KOH, Rb_2CO_3 and Cs_2CO_3, 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. HBF_4. 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 P_2O_5 at a temperature of 40–50°C. $NaBF_4$ was crystallized from a solution obtained in the neutralization of NaOH by means of 40% aq. HBF_4 and concentrated under vacuum. Powder diffraction patterns of the anhydrous salts were in accord with ASTM standards: $NaBF_4$ 11-571, $RbBF_4$ 18-1131, $CsBF_4$ 9-394, $Ca(BF_4)_2$ 14-508, $Sr(BF_4)_2$ 14-509, $Ba(BF_4)_2$ 19-138. We had no $LiBF_4$ standard available, and the KBF_4 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 an atmosphere of purified nitrogen at temperatures determined from thermoanalytical curves.

Results and discussion

The results of thermogravimetric analysis were used for determining the mass losses corresponding to the decomposition, to the temperature of the beginning of decomposition, and to the maximum rate of mass loss. Temperatures corresponding to the maxima of thermal effects were determined from the DTA curve. The results are shown in Table 1. It can be seen that two types of decomposition may be distinguished. One of them occurs with the following salts: $LiBF_4$, $Ca(BF_4)_2$, $Sr(BF_4)_2$ and $Ba(BF_4)_2$. The decomposition is effected in the solid phase with formation of gaseous BF_3 and solid fluoride according to the following equations:

$$M^{I}BF_4 \rightarrow MF+BF_3 \tag{1}$$

$$M^{II}(BF_4)_2 \rightarrow MF_2+2BF_3 \tag{2}$$

It has been found that these decomposition proceed in a single stage. Analysis of the TG and DTG curves as well as the furnace decomposition did not confirm the formation of unstable $BaBF_5$ suggested in the literature [1]. A thermal curves of $Ba(BF_4)_2$, which are characteristic of this type of decomposition, are shown in Fig. 1.

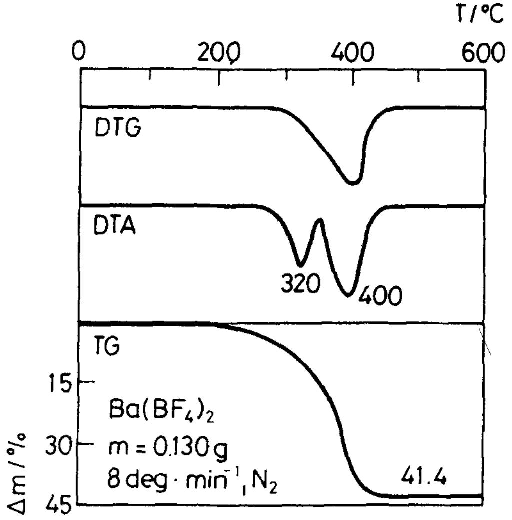

Fig. 1 TG, DTG and DTA curves of $Ba(BF_4)_2$

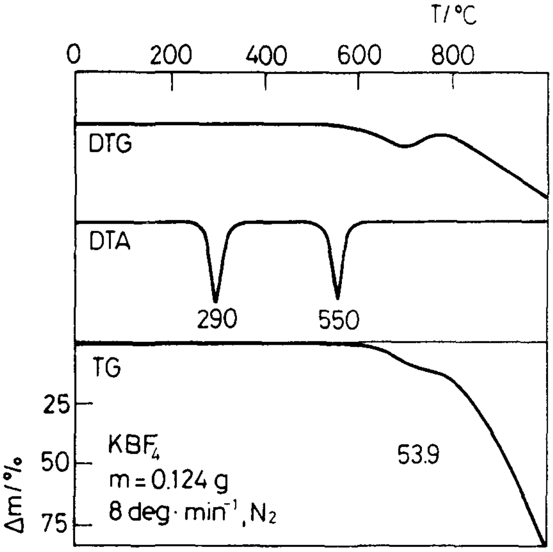

Fig. 2 TG, DTG and DTA curves of KBF$_4$

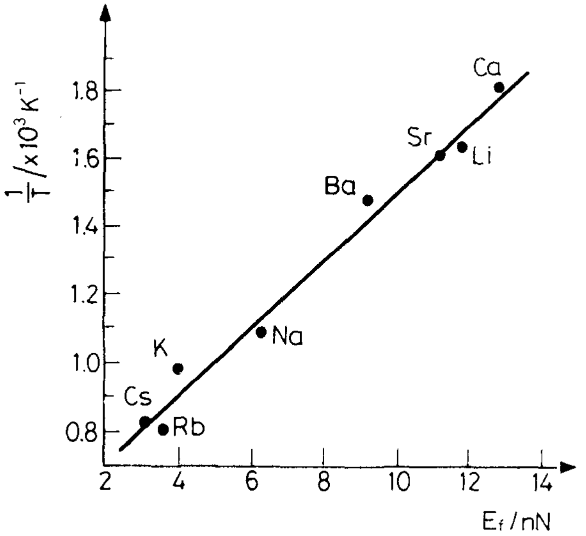

Fig. 3 Relationship between the reciprocal of T_{max} of the decomposition of fluoroborates and electronegativity force

Fluoroborates of sodium, potassium, rubidium and caesium undergo, on heating, polymorphic transformations at temperatures 240, 290, 240 and 165°C, respectively. Then they melt and the decomposition proceeds in the liquid phase. Sodium fluoroborate decomposes with formation of solid NaF and

Table 1 Results of thermogravimetric analysis of fluoroborates

Salt	Temperature range/°C	TG/mass loss/% observed	TG/mass loss/% theoretical	DTG T_{max}	DTA* T_{max}	Gaseus products	Solid products
$LiBF_4$	160–350	69.3	72.33	340	340 *d*	BF_3	LiF
$NaBF_4$	450–700			650	240 *p*	BF_3	NaF
					370 *m*		
					650 *d*		
KBF_4	550–~800	~20.0	53.86	~750	290 *p*	BF_3	KF, KBF_4
					550 *m*		
	700–1000	90.3	–	950		BF_3	KF
$RbBF_4$	550–1000	100.0	–	980	240 *p*	BF_3, $RbBF_4$	–
					550 *m*		
$CsBF_4$	550–1000	94.8	–	950	165 *p*	BF_3, $CsBF_4$	CsF
					530 *m*		
$Ca(BF_4)_2$	170–290	61.0	63.47	280	285 *d*	BF_3	CaF_2
$Sr(BF_4)_2$	200–360	50.9	51.91	350	350 *d*	BF_3	SrF_2
$Ba(BF_4)_2$	270–420	41.4	43.61	405	320 *m*	BF_3	BaF_2
					410 *d*		

*Abbreviations used in DTA column: *d*– decomposition, *m*–melting and *p*–polymorphic transformation. All effects were endothermic.

gaseous BF_3. A similar situation occurs in the decomposition of KBF_4, but in this case the evaporation of the salt is observed above 700°C. The decomposition of caesium and rubidium fluoroborates proceeds almost simultaneously with the evaporation of the salts thus making impossible the separation of the two processes. For this reason the mass losses recorded in the course of decomposition of KBF_4, $CsBF_4$ and $RbBF_4$ strongly exceed those calculated for reaction 1. The gaseous products identified during the decomposition processes are given in Table 1. Figure 2 shows TG, DTG and DTA curves recorded for KBF_4. The superposition of the decomposition process with evolution of BF_3 on one side and evaporation of KBF_4 is seen on the TG curve.

Based on the temperatures of maximum rate of mass loss and on the values of electronegativity forces of individual cations given in our previous paper [7] we have constructed a plot shown in Fig. 3. A linear relationship is seen between the reciprocal of the absolute temperature and the electronegativity force. The relationship may be described in terms of the following equation:

$$1/T_{max}\ [\mathrm{K}] = 1/1690\ \mathrm{K} + 8.58\cdot 10^{-5}\cdot E_f$$

The most diverging points are those corresponding to $CsBF_4$ and $RbBF_4$, but this fact seems to be the result of the above-mentioned superposition of two processes – decomposition and vaporisation. The correlation coefficient was as high as $r=0.997$. Taking into account the fact that a similar correlation was obtained for fluorosilicates [7] it seems reasonable to assume that the electronegativity force describes very well (in a quantitative manner) the acidic properties of cationic counterions. Table 2 contains experimentally determined and calcu-

Table 2 Temperature of maximum mass loss in the course of decomposition of fluoroborates comparison of measured and calculated values according to equation: $1/T_{max}\ [\mathrm{K}] = 1/1690\ \mathrm{K} + 8.58\cdot 10^{-5}\cdot E_f$

Cation	E_f/nN	T_{max}/°C		ΔT
		measured	calculated	
Li^+	11.8	340	322	18
Na^+	6.3	650	609	41
K^+	4.0	750	838	88
Rb^+	3.6	980	891	89
Cs+	3.1	950	962	12
Ba^{2+}	9.2	405	431	26
Sr^{2+}	11.2	350	345	5
Ca^{2+}	12.8	280	290	10
Zn^{2+}	32.5	–	–6	–
Cd^{2+}	22.4	–	93	–

lated values of decomposition temperature, along with the values anticipated for anhydrous fluoroborates of cadmium and magnesium.

Hence one can predict that whenever anhydrous $Cd(BF_4)_2$ will be obtained it should be stable at room temperature. Efforts of this type will be the subject of future studies.

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Zusammenfassung — Es wurde die thermische Zersetzung der wasserfreien Fluoroborate MBF_4 (M=Li, Na, K, Rb, Cs) und $M(BF_4)_2$ (M =Ca, Sr, Ba) untersucht. Die Zersetzung verläuft gemäß eines einfachen Säure-Basen-Mechanismus unter Freisetzung von BF_3. Der Einfluß der durch die Elektronegativität ausgedrückten Acidität des kationischen Gegenions auf den Weg der thermischen Zersetzung wurde quantitativ abgeschätzt.