

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry



journal homepage: www.elsevier.com/locate/fluor

Thermoanalytical and preparative investigations of the decomposition of potassium perfluoroorganyl(fluoro)borate salts, $K[R_FBF_3]$ (R_F = perfluoroalkyl, -alkenyl, -alkynyl, and -aryl groups) and $K[(R_F)_2BF_2]$ (R_F = C_6F_5 and C_6F_{13})

CrossMark

Vadim V. Bardin^a, Inna K. Shundrina^a, Hermann-Josef Frohn^{b,*}

^a N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, Acad. Lavrentjev Avenue 9, 630090 Novosibirsk, Russian Federation ^b Inorganic Chemistry, University of Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg, Germany

ARTICLE INFO

Article history: Received 18 October 2013 Received in revised form 6 November 2013 Accepted 7 November 2013 Available online 15 November 2013

Keywords: Potassium perfluoroorganyl(fluoro)borates Thermal decomposition TA analysis NMR spectroscopy

ABSTRACT

Potassium perfluoroalkenyl(fluoro)borates, K[R_FBF₃], (R_F = CF₂=C(CF₃), *cis*-CF₃CF=CF, and *cis*-C₆F₁₃CF=CF) decomposed at 208–225 °C (T_{max} , dTG). The K[R_FBF₃] salts (R_F = C₃F₇, C₆F₁₃, *trans*-CF₃CF=CF, and *trans*-C₄F₉CF=CF) decomposed at 273–312 °C (T_{max} , dTG). Both groups of salts formed volatile polyfluoroorganics and K[BF₄] as solid residue. The preparative thermolysis of selected prototypical salts K[R_FBF₃] showed that the polyfluoroorganics consisted of a mixture of internal perfluorohexenes, C₆F₁₂, and 1-H-tridecafluorohexane, C₆F₁₃CF=CFB₃]. The salts K[(C₆F₁₃BF₃], and of perfluorootypis, C₈F₁₄, and *cis*-C₆F₁₃CF=CFH in case of K[*cis*-C₆F₁₃CF=CFB₇]. The salts K[(C₆F₅)₂BF₂] and K[R_FBF₃] (R_F = CF₃=CC, C₁G₇=CC, C₆F₅, C₅C, C₅C₅, C₅, C₅NF₄) decomposed in the temperature range 249–337 °C (T_{max} , dTG) and mainly resulted in non-volatile polyfluoroorganics besides K[BF₄]. The reaction path of the thermolysis of perfluoroalkyl-, perfluoroalkenyl-, and perfluorophenyl-(fluoro)borates is discussed and compared with that of perfluoroacroboxylates.

© 2013 Published by Elsevier B.V.

1. Introduction

The first representatives of perfluoroorganyl(fluoro)borates were prepared more than 40 years ago. The majority of these compounds were synthesized during the last two decades. There are several reviews which cover the syntheses, chemical properties, spectral data, and application of these salts, e.g., in cross coupling reactions, in electrolytes of lithium ion batteries, or in supercapacitors for energy storage [1–7]. Data of their thermal properties, especially their decomposition, are very limited and usually reduced to their melting or decomposition points. In few cases more information was presented, e.g., the salts M[CF₃BF₃] decomposed in vacuum forming CF₂=CF₂ and M[BF₄] (M = K, 330-350 °C; M = NH₄; 175 °C) [8]. Chambers and Chivers reported that the thermal decomposition of K[C₆F₅BF₃] occurred in vacuum at ca. 300 °C and produced K[BF₄] and probably a mixture of perfluoroterphenyls [9]. The same authors published melting points of 324 °C for K[C₆F₅BF₃] [9] whereas Molander reported >250 °C [10]. The salts $K[(C_2F_5)_3BF]$ and $K[(CF_2=CF)_3BF]$ were characterized either by a melting point of 174 °C [11] or a

E-mail address: h-j.frohn@uni-due.de (H.-J. Frohn).

decomposition point of 84.9 °C [12], respectively. Zhou et al. determined a temperature range of decomposition of 270–320 °C for a series of perfluoroalkyl(trifluoro)borate salts $M[C_nF_{2n+1}BF_3]$ (M = K, Et₄N [13] (n = 2–4), cyclic quaternary ammonium [14], and 1-alkyl(alkyl ether)-3-methylimidazolium [15]). The salts $M[CF_3BF_3]$ (M = 1-alkyl(alkyl ether)-3-methylimidazolium) decomposed at lower temperatures (200–240 °C), presumably, via elimination of difluorocarbene [15]. The decomposition of those substances gave complex DSC data and products were not analyzed [13–15].

Very recently we investigated the thermal property of neat [4- $FC_6H_4N_2$][R_FBF_3] ($R_F = C_6F_5$, C_6F_{13} , *trans*- $C_4F_9CF=CF$, *cis*- $C_6F_{13}CF=CF$, $CF_3C=CC$) or their mixtures with NaF which gave the principal product 1,4- $C_6F_2H_4$ besides R_FBF_2 or Na[R_FBF_3], respectively, when heated above 120–160 °C [16]. The thermolysis of [4- $FC_6H_4N_2$][(C_6F_{13})₂BF₂] in NaF resulted in 1,4- $C_6F_2H_4$, Na[(C_6F_{13})₂BF₂], the isomer Na[(C_6F_{13})(C_5F_{11})(C_5F_{13}], and Na[BF₄]. Certainly, that the decomposition proceeded in the manner of the Balz–Schiemann reaction [16].

In the present work we report the thermal decomposition of a representative series of potassium perfluoroorganyl(trifluoro)-borates, K[R_FBF₃] (R_F = perfluorinated alkyl, alkenyl, alkynyl, and aryl group), and K[(R_F)₂BF₂] (R_F = C₆F₅, C₆F₁₃) by simultaneous thermogravimetry and differential scanning calorimetry (TG/

^{*} Corresponding author. Tel.: +49 2152 7868.

^{0022-1139/\$ –} see front matter © 2013 Published by Elsevier B.V. http://dx.doi.org/10.1016/j.jfluchem.2013.11.006

DSC) and for selected salts, by visually controlled preparative micro-scale thermolysis.

2. Results

2.1. Thermoanalytical investigation of potassium perfluoroalkyl(fluoro)borates

Thermal decomposition data of K[C₃F₇BF₃], K[C₆F₁₃BF₃], and K[(C₆F₁₃)₂BF₂] are summarized in Table 1. K[C₃F₇BF₃] melted at 299 °C (*T*_{onset}, DSC) followed by decomposition at 312 °C (*T*_{max}, dTG). The elongation of the perfluoroalkyl chain in K[C₆F₁₃BF₃] was accompanied by a decrease of the melting point to 285 °C and of the decomposition temperature to 303 °C. In contrast, borate K[(C₆F₁₃)₂BF₂] was thermally more stable and the melting at 354 °C overlapped remarkably with the decomposition at 363 °C. Before melting, borates K[C₆F₁₃BF₃] and K[(C₆F₁₃)₂BF₂] underwent solid–solid phase transitions. In case of all three perfluoroalkyl(trifluoro)borate salts, the decomposition proceeded with the formal elimination of the corresponding perfluoroalkene (Eqs. (1) and (2)) and the formation of K[BF₄] based on the TG data.

$$\mathbf{K}[\mathbf{C}_{n}\mathbf{F}_{2n+1}\mathbf{B}\mathbf{F}_{3}] \to \langle \mathbf{C}_{n}\mathbf{F}_{2n} \rangle + \mathbf{K}[\mathbf{B}\mathbf{F}_{4}] \tag{1}$$

 $K[(C_6F_{13})_2BF_2] \rightarrow \langle 2C_6F_{12} \rangle + K[BF_4]$ (2)

2.2. Thermoanalytical investigation of potassium perfluoroalkenyl(trifluoro)borates

The data of the thermal decomposition of the potassium perfluoroalkenyl(trifluoro)borate salts are summarized in Table 2. The thermogram of K[*cis*-CF₃CF=CFBF₃] contained an endothermic effect at T_{onset} = 131 °C (DSC) which corresponds to the melting point (proved by the visual melting point), two exothermic effects in the range 208–228 °C and an endothermic effect at 294 °C. The thermolysis was accompanied with a mass loss of 43% and ended with the formation of K[BF₄]. The latter was characterized with DSC by its endothermic phase transition from orthorhombic (α -K[BF₄]) to cubic (β -K[BF₄]) [17]. The phase transition data are in agreement with that of neat K[BF₄] (our data of an independent experiment).

From DSC the decomposition temperature of K[*cis*-C₆F₁₃-CF=CFBF₃] is only slightly lower than that of K[*cis*-CF₃CF=CFBF₃]. CFBF₃]. At the visual melting point of 184–186 °C a liquid phase appeared which above 190 °C showed bubbling of gas. According to the TG data, the decomposition began at 173 °C ($T_{3\%}$, dTG) with T_{max} = 208 °C (dTG). The endothermic effect at 121 °C will be attributed to a preceding solid–solid phase transition. The decomposition process is accompanied by a weak exothermic peak at ca. 208 °C and resulted in the solid residue K[BF₄]. The amount of volatiles determined from TG agrees with the expected mass loss.

Table 1

TG/DSC data of potassium perfluoroalkyl(fluoro)borates.

The visually controlled heating of K[*trans*-CF₃CF=CFBF₃] showed changes of the crystals at 115–119 °C which were followed by melting at 183–185 °C. These observations correspond to the two endothermic solid–solid phase transitions at 107 and 112 °C and the endothermic melting point at 171 °C (DSC). The molten salt decomposed exothermically above 223 °C ($T_{3\%}$, dTG) with T_{max} = 273 °C (dTG). Notably, the sequence of individual steps resembles that of the isomeric borate, K[CF₂=C(CF₃)BF₃], but all steps in the latter proceed at ca. 30 °C lower temperatures. Thus, there are two solid–solid phase transitions at 74 and 82 °C, followed by subsequent melting at 142 °C, and decomposition at 209 °C (T_{max} , dTG). The visual controlled mp of K[CF₂=C(CF₃)BF₃] was found at 143–145 °C.

Salt K[*trans*-C₄F₉CF=CFBF₃] melted at 184–187 °C (visually) and 176 °C (T_{onset} , DSC). The decomposition occurred at 287 °C (T_{max} , dTG). In all four potassium perfluoroalkenyl(trifluoro)borates, the decomposition was accompanied by the elimination of volatile perfluoroorganics according to Eq. (3) and K[BF₄] resulted as solid residue.

$$\mathbf{K}[\mathbf{C}_{n}\mathbf{F}_{2n-1}\mathbf{B}\mathbf{F}_{3}] \to \langle \mathbf{C}_{n}\mathbf{F}_{2n-2} \rangle + \mathbf{K}[\mathbf{B}\mathbf{F}_{4}] \tag{3}$$

2.3. Thermoanalytical investigation of potassium perfluoroalkynyl(trifluoro)borates

The TG–DSC data of potassium perfluoroalkynyl(trifluoro)borates are summarized in Table 3. The decomposition of $K[C_3F_7C\equiv CBF_3]$ started directly after melting ($T_{onset} = 217$ °C, DSC) and went via two steps with $T_{max} = 228$ and 272 °C (dTG). A similar picture was obtained for the isomeric borate $K[(CF_3)_2CFC\equiv CBF_3]$ but with melting and decomposition ca. 20– 30 °C higher. The mass loss for both salts corresponded with the elimination of "C₅F₆" and the formation of K[BF₄] as solid residue (Eqs. (4) and (5)).

$$\mathbf{K}[\mathbf{C}_{3}\mathbf{F}_{7}\mathbf{C} \equiv \mathbf{C}\mathbf{B}\mathbf{F}_{3}] \to \langle \mathbf{C}_{5}\mathbf{F}_{6} \rangle + \mathbf{K}[\mathbf{B}\mathbf{F}_{4}] \tag{4}$$

$$K[(CF_3)_2 CFC \equiv CBF_3] \rightarrow \langle C_5 F_6 \rangle + K[BF_4]$$
(5)

Heating of K[CF₃C=CBF₃] in a Koffler Block melting apparatus between two glass disks showed a melting point at 183–187 °C and parallel the formation of a dark brown solid. The DSC data reveal two endothermic effects, a solid–solid phase transition ($T_{onset} = 115$ °C) and melting ($T_{onset} = 178$ °C). Further heating caused an intensive exothermic process ($T_{max} = 249$ °C, dTG) which, however, was accompanied by a remarkable small mass loss (only 7%).

Heating of borate K[CF₃CF=CFC≡CBF₃] was characterized by an exothermic process (T_{max} = 273 °C (dTG)) and was accompanied by a partial eruption of the probe (initial mass 3.131 mg) through the pierced lid. Using a smaller probe (1.983 mg) we measured a remarkable small mass loss (9%). Notably, that a second heating scan to 400 °C after cooling to 28 °C at the end of the first measurement proceeded without mass loss and displayed only an

Compound	T^1_{s-s} , °C	$T_{ m melting}$, °C	Decomposition					
			$T_{3\%}^{b} \circ C$ $T_{max}^{c} \circ C$ Heat effect of decomposition		Mass loss, %			
						$\Delta m_{\rm exp}$	$\Delta m_{\rm calc}{}^{\rm d}$	
K[C ₃ F ₇ BF ₃]	-	299	303	312	Exothermic	57	54	
$K[C_6F_{13}BF_3]$	255	285	271	303	Exothermic	72	71	
$K[(C_6F_{13})_2BF_2]$	327	354	290	363	Exothermic	89	83	

^a Temperature of solid-solid phase transition.

^b Temperature of 3% mass loss.

^c Temperature of the rate maximum of the decomposition.

^d Calculated from the residue for K[BF₄].

Table 2			
TCIDCC	4.4.4.4	of moto solum	

TG/DSC data of potassium perfluoroalkenyl(trifluoro)borates.

Compound	T^1_{s-s} , ^a °C	$T^2_{\mathrm{S-S}}$, °C	$T_{ m melting}$, °C	Decomposition					
				<i>T</i> _{3%} , ^b °C	T_{\max} , °C	Heat effect of decomposition	Mass loss, %		T_{s-s} , °C
							$\Delta m_{\rm exp}$	$\Delta m_{\rm calc}^{\rm d}$	
K[cis-CF ₃ CF=CFBF ₃]	-	_	131	173	225	Exothermic	43	53	294
K[cis-C ₆ F ₁₃ CF=CFBF ₃]	121	-	184–186 ^f	173	208	Exothermic	71	74	288
K[trans-CF ₃ CF=CFBF ₃]	107	112	171	223	273	Exothermic	43	47	292
K[trans-C ₄ F ₉ CF=CFBF ₃]	-	-	176	268	287	Exothermic	67	68	-
$K[CF_2=C(CF_3)BF_3]$	74	82	142	173	209	Exothermic	39	47	287

Temperature of solid-solid phase transition.

^b Temperature of 3% mass loss.

Temperature of the rate maximum of the decomposition.

^d Calculated from the residue for K[BF₄]. Solid-solid phase transition (α -K[BF₄] $\rightarrow \beta$ -K[BF₄]).

f Visually.

endothermic peak at 288 °C, which can be attributed to the transition of α -K[BF₄] to β -K[BF₄]. In the case of K[CF₃C=CBF₃] which was also characterized by an unexpected low mass loss of 7%, the second heating scan of from 28 to 400 °C displayed a similar result.

The DSC result of $K[C_6F_5C \equiv CBF_3]$ showed no thermal process below 219 °C. Above that temperature DSC presented an ambiguous result: which can be attributed to either two exothermic maxima at 278 °C and 294 °C or one broad exothermic maximum which has been superposed by an endothermic minimum at 284 °C. The endothermic effect may belong to the solid-solid phase transition of obtained K[BF₄]. The experimental mass loss Δm_{exp} (20%) was significantly lower than the calculated Δm_{calc} (58%) which may indicate that thermally stable, non-volatile fluoroorganic materials have resulted till 370 °C from borate $K[C_6F_5C \equiv CBF_3].$

2.4. Thermoanalytical investigation of potassium perfluoroaryl(fluoro)borates

The TG data of potassium perfluoroaryl(fluoro)borates are summarized in Table 4. The DSC curve of K[C₆F₅BF₃] contained two weak endothermic effects at 170 and 210 $^{\circ}$ C (T_{onset}) which correspond to phase transitions. Those assignments were confirmed by heating under visual control. At 327 $^{\circ}$ C (T_{max} , DSC) an exothermic process took place. The process was accompanied by a gradual mass loss which achieved 19% at 410 °C. Cooling to 28 °C followed by a second heating to 400 °C showed no mass loss and no

Table 3

TG/DSC data of potassium perfluoroalkynyl(trifluoro)borates.

thermal process except the solid-solid phase transition of K[BF₄] $(T_{\text{onset}} = 288 \,^{\circ}\text{C}, \, \text{DSC}).$

Borate $K[(C_6F_5)_2BF_2]$ underwent a fast decomposition and the TG diagram revealed that the mass loss proceeded in two steps at 327 and 332 °C (T_{max}) with a total mass loss of 46% till 470 °C.

Two thermal processes were found in the DSC result of K[2,3,5,6-C₅NF₄BF₃]. The first was a solid-solid phase transition $(T_{\text{onset}} = 148 \text{ °C})$. Heating of the salt under visual control displayed a change of the solid at 155-161 °C. The second process at $T_{\rm max}$ = 337 °C (dTG) was caused by decomposition and accompanied by a 33% mass loss.

All studied potassium perfluoroarvl(fluoro)borates have in common that no melting could be detected in the DSC measurement. Furthermore, the thermal decomposition of all three salts is characterized by a remarkable lower experimental mass loss Δm_{exp} related to the calculated value based on the idealized Eq. (6).

$$K[R_FBF_3] \rightarrow \langle R_F' \rangle + K[BF_4]$$
 (6)

2.5. Preparative thermolysis of selected potassium perfluoroorganyl(trifluoro)borates

The TA data display the range of thermal stability of perfluoroorganyl(fluoro)borates but give neither information of the routes of decomposition nor of the nature of the polyfluoroorganic products. To get insight into the kind of products, we performed preparative thermolysis reactions of three selected

Compound	T^1_{s-s} , ^a °C	$T_{ m melting}$, °C	Decomposition						
			<i>T</i> _{3%} , ^b ∘C	T _{max} , ^c ∘C	Heat effect of decomposition	Mass loss, %		$T_{\alpha-\beta}$, • • C	
						$\Delta m_{\rm exp}$	$\Delta m_{\rm calc}{}^{\rm d}$		
$K[CF_3C \equiv CBF_3]$	115	178	242	249	Exothermic	7	37	296	
$K[CF_3C \equiv CBF_3]^f$	-	-	-	-	-	0	-	289	
$K[C_3F_7C \equiv CBF_3]$	-	217	228	228, 272	Exothermic	49 ^g	58	286	
$K[(CF_3)_2CFC \equiv CBF_3]$	-	245	255	258, 283, 290	Exothermic	54 ^g	58	284	
$K[CF_3CF=CFC=CBF_3]$	161	-	262	273	Exothermic	9	52	-	
K[CF ₃ CF=CFC=CBF ₃] ^f	-	-	-	-	-	0	-	288	
$K[C_6F_5C \equiv CBF_3]$	-	-	222	241, 293	Exothermic	20	58	284 ^h	

^a Temperature of solid-solid phase transition.

Temperature of 3% mass loss.

Temperature of the rate maximum of the decomposition.

Calculated from the residue for K[BF₄].

Solid-solid phase transition (α -K[BF₄] $\rightarrow \beta$ -K[BF₄]).

f The sample was cooled after the first scan to 28 °C and again heated to 400 °C.

Heating up to 400 °C.

h Proposed assignment.

Table 4				
TG/DSC data	of potassium	perfluoroaryl	(fluoro)borates.

Compound ^a	T^1_{s-s} , °C	T^2_{s-s} , °C	Decomposition					
			<i>T</i> _{3%} , ^c ∘C	T_{\max} , ^d °C	Heat effect of	Mass loss, %		$T_{\alpha-\beta}$, ^f °C
					decomposition	Δm_{exp}	$\Delta m_{\rm calc}^{\rm e}$	
K[C ₆ F ₅ BF ₃]	170	210	328	329	Exothermic	19 ^g	54	_
K[C ₆ F ₅ BF ₃] ^h	-	-	-	-	-	0	-	288
$K[(C_6F_5)_2BF_2]$	-	-	315	327, 332	Exothermic	46 ⁱ	70	-
K[2,3,5,6-C ₅ NF ₄ BF ₃]	148	-	316	337	Exothermic	33	51	-

^a No melting was detected.

^b Temperature of solid-solid phase transition.

^c Temperature of 3% mass loss.

^d Temperature of the rate maximum of the decomposition.

^e Calculated from the residue for K[BF₄].

^f Solid–solid phase transition (α -K[BF₄] \rightarrow β -K[BF₄]).

^g Heating up to 410 °C.

^h The sample was cooled after the first scan to 28 °C and again heated to 400 °C.

ⁱ Heating up to 470 °C.

potassium perfluoroorganyl(trifluoro)borates: $K[C_6F_{13}BF_3]$, $K[cis-C_6F_{13}CF=CFBF_3]$, and $K[C_6F_5BF_3]$, with a thermal behavior which is typical for groups of borates. Reactions were performed in flamedried sealed glass ampoules at decomposition temperatures slightly exceeding T_{offset} obtained from DSC measurements.

The decomposition of $K[C_6F_{13}BF_3]$ at 300–310 °C (bath) was not completed within 40 min and gave a mixture of internal perfluorohexenes and 1-H-tridecafluorohexane. Perfluorohex-1-ene was not detected (Scheme 1).

The decomposition of K[*cis*-C₆F₁₃CF=CFBF₃] occurred incompletely at 215–225 °C (bath) within 1.5 h and gave *cis*-C₆F₁₃CF=CFH, C₆F₁₃C=CF, and C₅F₁₁C=CCF₃ besides not identified perfluoroorganics. According to ¹⁹F NMR and GC–MS data, the latter may be dimers of perfluorooctyne. The compounds *trans*-C₆F₁₃CF=CFH, C₅F₁₁CF=CFCF₂H, and C₅F₁₁CF=C=CF₂ were not formed (Scheme 2).

Thermolysis of K[C₆F₅BF₃] at 325–335 °C (bath) for 40 min gave a black solid which was extracted with DMF. The ¹⁹F NMR spectrum of the extract contained signals of K[BF₄], C₆F₅H (trace), and three groups of resonances at -136 to -140, -149 to -151 and -161 ppm in the ratio 100:15:65. The latter compound(s) probably represent(s) perfluorinated polyphenyl derivatives such as K[C₆F₅(C₆F₄)_nBF₃]. In the proposed assignment the resonances of the BF₃ group are overlapping with aryl fluorine signals at 136– 140 ppm. Such an overlap is observed for K[C₆F₅BF₃] in DMF [18]. The insoluble part of the reaction mixture was not studied in detail.

3. Discussion

The investigated potassium perfluoroorganyl(fluoro)borates can be subdivided into two groups. The first group of borates melts and undergoes subsequently decomposition into volatile perfluoroorganic products and a solid residue which consists of K[BF₄]. In some cases T_{mp} and T_{dec} are very close together. The first group is typical for perfluoroalkyl(fluoro)borates, perfluoroalk-enyl(trifluoro)borates, and perfluoroalkynyl(trifluoro)borates (except for K[CF₃CF=CFC=CBF₃] and K[C₆F₅C=CBF₃]). Within this group perfluoroalkyl(trifluoro)borates are thermally more stable than alkenyl(fluoro)borates. Within the subgroup of perfluoroalk-enyl(fluoro)borates *trans*-perfluoroalkenyl(trifluoro)borates are more stable than their *cis*-isomers. The subgroup of potassium perfluoroalkynyl(trifluoro)borates, K[R_FC=CBF₃] (R_F = CF₃, C₃F₇, (CF₃)₂CF), decompose in the temperature range of 228–290 °C.

The present investigation allows giving a sequence of the temperature of the rate maximum of decomposition (T_{max} , dTG) of K[R_FBF₃] salts: K[2,3,5,6-C₅NF₄BF₃] (337 °C) ~ K[C₆F₅BF₃] (329 °C) > K[C₃F₇BF₃] (312 °C) ~ K[C₆F₁₃BF₃] (303 °C) > K[trans-C₄F₉CF=CFBF₃] (287 °C) > K[trans-CF₃CF=CFBF₃] (273 °C) ~ K[CF₃CF=CFC=CBF₃] (272 °C) > K[(CF₃)₂CFC=CBF₃] (258 °C) ~ K[CF₃CE=CBF₃] (249 °C) ~ K[C₆F₅CE=CBF₃] (241 °C) > K[cis-CF₃CF=CFBF₃] (225 °C) > K[CF₂ ==C(CF₃) BF₃] (209 °C) ~ K[trans-C₆F₁₃CF=CFBF₃] (208 °C).

The reaction pathway of the first group can be described by the sequence: (a) heterolytic cleavage of C–B bond, (b) elimination of fluoride from the perfluoroorganyl anion in $\langle K[R_F] \rangle$, (c) fluoride transfer from KF to BF₃. Final products are simplified perfluoroalk-enes (from perfluoroalkyl(trifluoro)borates) and perfluoroalkynes (from perfluoroalkenyl(trifluoro)borates) besides K[BF₄]. This generalization and idealization is supported by the results of the preparative thermolysis of K[C₆F₁₃BF₃] and K[*cis*-C₆F₁₃CF=CFBF₃]. $\langle K[R_F] \rangle$ eliminates KF spontaneously to give the terminal perfluoroalkene. Isomerization of the latter ends up in the observed

58% conversion

C₅F₁₁C≡CCF₃ + K[BF₄] + ...

Scheme 2.

V.V. Bardin et al./Journal of Fluorine Chemistry 157 (2014) 73-78



internal perfluorohexenes. In a side-reaction, the perfluorocarbanion in $\langle K[R_F] \rangle$ reacts with an H⁺-donor (glass wall, etc.) to yield 1-H-perfluoroalkane (Scheme 3).

The thermal decomposition of potassium perfluoroalkenyl(trifluoro)borates can formally be described in a similar manner (Scheme 4).

Notably, that R_FH which derived from the corresponding key carbanion intermediate $[R_F]^-$ was unambiguously proved in both cases.

The thermolysis reactions of potassium perfluoroalkyl(trifluoro)borates and perfluoroalkenyl(trifluoro)borates are formally related to the known thermal decarboxylation of potassium perfluoroalkylcarboxylates and perfluoroalkenylcarboxylates where perfluoroalkenes and a mixture of perfluoroalkynes and perfluoroalkadienes were produced, respectively [19]. In the thermolysis of potassium perfluoroalkylcarboxylates, K[R_FCO₂], potassium perfluoroalkalide, K[R_F], is the proposed intermediate.

The decomposition of salts which belong to the second group (without melting point), such as $K[CF_3CF=CFC==CBF_3]$, $K[C_6F_5C==CBF_3]$, $K[C_6F_5C==CBF_3]$, $K[C_6F_5C==CBF_3]$, $K[C_6F_5DF_3]$, $K[(C_6F_5)_2BF_2]$, and $K[2,3,5,6-C_5NF_4BF_3]$ is characterized by a significantly lower amount of volatile fluoroorganics than expected. But $K[BF_4]$ was formed too. The result of the preparative thermolysis of $K[C_6F_5BF_3]$ allows to assume the formation of perfluoropolyphenyl(trifluoro)borates, $K[C_6F_5(C_6F_4)_nBF_3]$ and/or $K[(C_6F_5)_nC_6F_{5-n}BF_3]$, at least in the DMF soluble fraction of the reaction extract (cf. [9]). Their formation can be explained by the generation of the pentafluorophenyl anion via the heterolytic carbon-boron bond cleavage and a successive nucleophilic polyarylation (Scheme 5).

4. Conclusion

The reaction path of the thermolysis of $K[R_FBF_3]$ salts depends on the nature of R_F . In case of R_F = perfluoroalkyl and perfluoroalk-1-en-1-yl perfluoroalkenes and -alkynes are formed as volatile products, respectively, besides K[BF₄] as solid residue. In case of R_F = perfluoroaryl, thermolysis proceeds without melting with a low amount of volatile products and nucleophilic pentafluorophenylation products $(R_F = C_6F_5)$ of the starting salt besides K[BF₄]. The thermolysis of K[$R_FC \equiv CBF_3$] salts is more complex and depends on the substituent R_F. It is scientifically interesting to compare the reaction path of the thermolysis of K[R_FBF₃] salts with that of the perfluoroorganylcarboxylates, $K[R_FCO_2]$. The thermolysis of the perfluoroalkyl(fluoro)borates resembles strongly that of perfluoroalkylcarboxylates. In case of perfluoroalkylcarboxyles perfluoroalkenes are formed besides KF and CO₂. In both cases cleavage of the strong C-C or C-B proceeds in the first step. The experimental finding that in case of fluoroorganyl-(fluoro)borate salts the thermal cleavage of the C-B bond is favored over fluoride abstraction from the B-F moiety allows to conclude that despite of the strong electrostatic interaction of the negatively charged BF₃⁻ moiety and K⁺ the fluoroorganyl(fluoro)borate anion in the salt decomposes as expected for the gas phase.

5. Experimental

The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (¹H at 300.13 MHz, ¹⁹F at 282.40 MHz). The chemical shifts are referenced to TMS (¹H), and CCl₃F (¹⁹F) [with C₆F₆ as a secondary reference (-162.9 ppm)]. The composition of the reaction mixtures and the yield of products were determined by

¹⁹F NMR spectroscopy using C₆F₆ as an internal quantitative standard. TG-DSC analyses were performed using a Netzsch STA409 instrument with a heating rate of 10 K/min under He flow. The solid samples (2-4 mg) were weighed into aluminum pans which were closed by a pierced aluminum lid. To support the assignment of endothermic processes (solid-solid phase transitions or melting) of DSC scans in addition the salts were analyzed visually using a Koffler melting point apparatus. Temperatures of phase transitions (T_{s-s} , $T_{melting}$) were determined from DSC curves as T_{onset} . Temperature of maximal rate of decomposition (T_{max}) was determined from the dTG diagrams.

Borates K[C₃F₇BF₃], K[C₆F₁₃BF₃] [20], K[(C₆F₁₃)₂BF₂] [16], K[trans-C₄F₉CF=CFBF₃] [21], K[*cis*-C₆F₁₃CF=CFBF₃] [21], K[*cis*-CF₃-CF=CFBF₃], K[trans-CF₃CF=CFBF₃] [22], K[CF₂=C(CF₃)BF₃] [23], $K[CF_3C \equiv CBF_3], K[C_3F_7C \equiv CBF_3], K[(CF_3)_2CFC \equiv CBF_3], K[CF_3CF = CF C \equiv CBF_3$, $K[C_6F_5C \equiv CBF_3]$ [24], $K[C_6F_5BF_3]$ [25], $K[2,3,5,6-C_5NF_4BF_3]$ [18], and $K[(C_6F_5)_2BF_2]$ [26] were prepared as described.

5.1. Thermolysis of $K[C_6F_{13}BF_3]$

The salt K[C₆F₁₃BF₃] (231 mg, 0.54 mmol) was sealed in a glass ampoule and deposited in a pre-heated (300 °C) metal bath. After 40 min at 300-310 °C the ampoule was cooled to 25 °C. The content, a gray powder, was extracted with CHCl₃ (0.8 mL). The ¹⁹F NMR spectrum contained the resonances of *cis*-C₃F₇CF=CFCF₃ [27], trans-C₃F₇CF=CFCF₃ [27], trans-C₂F₅CF=CFC₂F₅ [27], and C₆F₁₃H [28] (molar ratio 21:49:1:29). After extraction with CHCl₃ the residue was dried on air and extracted with DMF (1.5 mL). The extract contained $K[C_6F_{13}BF_3]$ (0.40 mmol, 26% conversion) besides K[BF₄] (0.03 mmol) (¹⁹F NMR).

5.2. Thermolysis of K[cis-C₆F₁₃CF=CFBF₃]

The salt K[cis-C₆F₁₃CF=CFBF₃](212 mg, 0.43 mmol) was sealed in a glass ampoule and deposited in a pre-heated (210 °C) metal bath. After 1.5 h at 215–225 °C, the ampoule was cooled to 25 °C and the organic products were extracted with CHCl₃ (0.8 mL). The ¹⁹F NMR spectrum contained resonances of *cis*-C₆F₁₃CF=CFH $(0.14 \text{ mmol}), C_6F_{13}C \equiv CF (0.02 \text{ mmol}), and C_5F_{11}C \equiv CCF_3$ (0.04 mmol). Products with resonances at δ –82, –105 to –112, -119, -122 to -124, and -127 ppm could not be identified. The GC-MS analysis showed the presence of 3 products (ratio 1:1.5:2) with equal mass-spectra which may be isomers of the dimers of perfluorooctyne (M^+ 724, $C_{16}F_{28}$). After extraction with CHCl₃ the residue was dried on air and extracted with DMF (1.5 mL). The extract contained K[cis-C₆F₁₃CF=CFBF₃] (0.18 mmol) besides the soluble part of K[BF₄].

5.3. Thermolysis of $K[C_6F_5BF_3]$

The salt $K[C_6F_5BF_3]$ (313 mg, 1.14 mmol) was sealed in a glass ampoule and deposited in a pre-heated (325 °C) metal bath. After 40 min at 325–335 °C the ampoule was cooled to 25 °C. The inner wall of the ampoule was coated with a dark solid material. The products were extracted with DMF (2 mL \times 0.5 mL). The extract was filtered through wool and gave a dark brown solution. The ¹⁹F NMR spectrum contained the resonances of C_6F_5H (trace), K[BF₄], and three groups of resonances at -136 to -140, -149 to -151, and -161 ppm in the ratio 100:15:65 besides weak multiplets at -55 and -127 ppm.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem. 2013.11.006.

References

- [1] G. Pawelke, H. Bürger, Appl. Organomet. Chem. 10 (1996) 147-174.
- [2] W.E. Piers, T. Chivers, Chem. Soc. Rev. 26 (1997) 345-354.
- G. Pawelke, H. Bürger, Coord. Chem. Rev. 215 (2001) 243-266.
- [4] T. Chivers, J. Fluorine Chem. 115 (2002) 1-8.
- [5] V.V. Bardin, H.-J. Frohn, Main Group Met. Chem. 25 (2002) 589-613.
- [6] M. Finze, E. Bernhardt, H. Willner, Angew. Chem. Int. Ed. 46 (2007) 9180–9196.
- [7] (a) N.Y. Adonin, V.V. Bardin, Russ. Chem. Rev. 79 (2010) 757-785; (b) N.Y. Adonin, V.V. Bardin, Usp. Khim. 79 (2010) 832-860.
- [8] R.D. Chambers, H.C. Clark, C.J. Willis, J. Am. Chem. Soc. 82 (1960) 5298-5301.
- [9] R.D. Chambers, T. Chivers, D.A. Pyke, J. Chem. Soc. (1965) 5144–5145.
- [10] G.A. Molander, B.J. Biolatto, J. Org. Chem. 68 (2003) 4302-4314.
- [11] G. Pawelke, H. Willner, Z. Anorg, Allg. Chem. 631 (2005) 759–762.
- [12] N.Yu. Adonin, V.V. Bardin, H.-J. Frohn, Organometallics 23 (2004) 535–539.
 [13] Z.-B. Zhou, M. Takeda, M. Ue, J. Fluorine Chem. 123 (2003) 127–131.
- [14] Z.-B. Zhou, H. Matsumoto, K. Tatsumi, Chem. Eur. J. 12 (2006) 2196-2212.
- [15] Z.-B. Zhou, H. Matsumoto, K. Tatsumi, Chem. Eur. J. 10 (2004) 6581–6591.
- [16] V.V. Bardin, H.-J. Frohn, J. Fluorine Chem. (2013), http://dx.doi.org/10.1016/ i.ifluchem.2013.08.001.
- [17] (a) G.S. Petrov, I.M. Volodkovich, R.A. Vecher, A.A. Vecher, Thermochim, Acta 87 (1985) 381 - 384:
 - (b) V.V. Volkov, K.G. Mvakishev, L.Ya. Solomatina, G.S. Voronina, Koord, Khim, 18 (1992) 497-502:
 - (c) V.V. Volkov, K.G. Myakishev, L.Ya. Solomatina, G.S. Voronina, Sov. J. Coord. Chem. 18 (1992) 429-434:
 - (d) K.S. Gavrichev, G.A. Sharpataya, V.E. Gorbunov, Thermochim. Acta 282-283 (1996) 225 - 238
 - (e) M. Finze, E. Bernhardt, H. Willner, C.W. Lehmann, J. Am. Chem. Soc. 127 (2005) 10712-10722
- [18] A.N. Abo-Amer, Yu. Adonin, V.V. Bardin, P. Fritzen, H.-J. Frohn, Ch. Steinberg, J. Fluorine Chem, 125 (2004) 1771-1778.
- [19] N. Lui, J. Fisher-Lui, in: B. Baasner, H. Hagemann, J.C. Tatlow (Eds.), Houben-Weyl Methods of Organic Chemistry. Organo-Fluorine Compounds, vol. E10b, Part 1, Thieme, Stuttgart, 4th ed., 2000, 691-709.
- [20] H.-J. Frohn, M. Giesen, D. Welting, V.V. Bardin, J. Fluorine Chem. 131 (2010) 922-936.
- [21] H.-J. Frohn, V.V. Bardin, Z. Anorg, Allg. Chem. 627 (2001) 2499-2500.
- [22] N.Yu. Adonin, V.V. Bardin, H.-J. Frohn, Main Group Met. Chem. 32 (2009) 153–159.
- [23] H.-J. Frohn, V.V. Bardin, Z. Anorg, Allg. Chem. 629 (2003) 2465-2470.
 - [24] V.V. Bardin, N.Yu. Adonin, H.-J. Frohn, Organometallics 24 (2005) 5311–5320.
- [25] N.Yu. Adonin, D.E. Babushkin, V.N. Parmon, V.V. Bardin, G.A. Kostin, V.I. Mashu-
- kov, H.-J. Frohn, Tetrahedron 64 (2008) 5920-5930. [26] N.Yu. Adonin, V.V. Bardin, H.-J. Frohn, Collect. Czech. Chem. Commun. 73 (2008)
- 1681-1690. [27] (a) T.I. Filyakova, M.I. Kodess, N.V. Peschanskii, A.Ya. Zapevalov, I.P. Kolenko, Zh. Org. Khim. 23 (1987) 1858-1866;
- (b) T.I. Filyakova, M.I. Kodess, N.V. Peschanskii, A.Ya. Zapevalov, I.P. Kolenko, J. Org. Chem. USSR (Engl. Transl.) 23 (1987) 1651-1658
- [28] T. Hudlicky, R. Fan, J.W. Reed, D.R. Carver, M. Hudlicky, E. Eger, J. Fluorine Chem. 59 (1992) 9-14.