Influence of structural factors on the thermolysis of 2-alkoxytetrafluoropropionic acid salts

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2,2,2-Trifluoroethyl and phenyl trifluorovinyl ethers were obtained by the thermolysis of 2-substituted potassium tetrafluoropropionates ROCF(CF_3)COOK (R = CF_3CH_2 ; Ph). The reaction mechanism is analyzed.

Key words: hexafluoropropylene oxide, 2-alkoxytetrafluoropropionic acids, 2-phenoxytetrafluoropropionic acid, alkyl trifluorovinyl ethers, phenyl trifluorovinyl ether.

Thermal decomposition of fluorocarboxylic acids is a universal method for the synthesis of higher linear fluoroolefins.^{1,2} A particular case of this reaction is the thermolysis of 2-alkoxytetrafluoropropionic acid salts ROCF(CF₃)COO⁻M⁺ (R = alkyl, α,α -dihydrofluoro-alkyl, perfluoroalkyl; M is metal cation) (1)^{3,4} resulting in trifluorovinyl ethers.

However, in the case of perfluorinated salts 1, perfluoroalkyl vinyl ethers that found practical use as comonomers in the synthesis of fluoropolymers are formed in almost quantitative yields,⁴ whereas the thermolysis of compounds 1 with R = Me, Et, and CF_3CH_2 leads to a complicated mixture of products.³ It was postulated³ that the composition of the reaction products reflects the competition between the decarboxylation accompanied by the β-elimination of the fluoride ion to form trifluorovinyl ethers and the intramolecular nucleophilic substitution of the α -fluorine atom with the intermediate formation of 2-alkoxy-2-trifluoromethyl-α-lactones, whose rate is determined by the influence of the alkoxy group. It was shown for the thermolysis of salts 1 (R = Me) as an example that the contribution of the latter direction of the process increased from 75-80% in the case of the potassium and cesium salts to 100% for the sodium salt. This is due to the "higher energy of formation of the crystalline lattice of NaF." ³ However, reasons for the preferential (in the case of the sodium salts, exclusive) α -elimination of the fluoride ion during the thermolysis of salts 1 remained beyond the discussion.

We do not contest the proposed³ scheme of thermolysis of salts 1 but believe that the influence of the nature of the alkoxy group and the counterion on the composition of the reaction products is determined by other factors, namely: (a) the anionoid mobility of the α -fluorine atom that increases in parallel to the electron-releasing ability of the RO group and (b) the ionic radius of the metal cation that exerts an electrophilic assistance of the elimination of F^- within the frame of the five- or six-membered transition state.

In order to confirm the above assumption, we synthesized 2-alkoxytetrafluoropropionic acids 2 by the reaction of the corresponding alcohols and an excess of alkali with hexafluoropropylene oxide (HFPO) in an ether—water system in the presence of $Bu_4N^+Br^-$; the acidification of the reaction mixture affords acids 2 in 40–70% yield (this procedure is a simplified version of the synthesis of 2-alkoxytetrafluoropropionic acids described earlier^{3,5}) (Scheme 1). Potassium salts **1a**–**c** were obtained by the treatment of acids **2** with aqueous KOH.

Scheme 1

$$CF_{3}CF_{-}CF_{2} \xrightarrow{1) \text{ ROH/aq, KOH, ~20 °C}} ROCFCOOH \xrightarrow{KOH} CF_{3} \xrightarrow{2} CF_{3} \xrightarrow{2} 2a-c$$

$$\xrightarrow{ROCFCOOK} \xrightarrow{\Delta} CF_{2} \xrightarrow{-CO_{2}, -KF} ROCF=CF_{2} \xrightarrow{3} 2a-c$$

$$1a-c$$

$$R = \text{Et (a), CF_{3}CH_{2} (b), Ph (c)}$$

The choice of alcohol was based on the fact that the electron-donating character of the RO group increases inversely to the acidity of the starting alcohol (the pK_a values for PhOH, CF₃CH₂OH, and EtOH are 9.98,⁶ 12.3,⁷ and 18.0,⁶ respectively) and, hence, the anionoid mobility

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Table	1.	Yields	of	ethers	3	obtained	by	the
thermo	olys	sis of sal	lts 1	L				

Salt	1	Yield of com		
R	М	pound 3 (%)		
Et	Na	0*		
	Κ	10		
CF ₃ CH ₂	Na	4*		
5 2	K	67		
Ph	K	63		

* See Ref. 3.

of the α -fluorine atom increases in the series of salts $\mathbf{1c} \approx \mathbf{1b} \ll \mathbf{1a}$. As shown by the thermolysis of these salts (see Scheme 1), the yields of trifluorovinyl ethers **3** decrease in the same sequence (Table 1).

The concept about the influence of the ionic radius of the cation on the yield of trifluorovinyl ethers (the ionic radii for Na⁺, K⁺, and Cs⁺ at the coordination number six are⁸ 0.95, 1.33, and 1.69 Å, respectively) makes it possible to explain the described³ increase in the yield of ether **3d** (R = Me) during the thermolysis of salts **1** with R = Me in the series of cations Na⁺, K⁺, and Cs⁺ (Scheme 2).

Scheme 2



In the case of the smallest Na⁺ ion, only the fivemembered transition state is formed in which the nucleophilic substitution of the α -fluorine atom occurs with the electrophilic assistance of Na⁺; no ether **3d** is formed. The formation of ether **3d** (26 and 20% yields) upon the thermolysis of the potassium and cesium salts, whose ionic radii are substantially larger, indicates a tendency to form the six-membered transition state, although the low yields of trifluorovinyl ether show that the reaction course is determined, to a great extent, by the anionoid mobility of the α -fluorine atom and the formation of α -lactone remains the predominant direction of thermolysis.

Experimental

 19 F NMR spectra were recorded on a Bruker 200SY instrument (188.3 MHz) in a CCl₄ solution (CF₃COOH as external standard).

2-(2,2,2-Trifluoroethoxy)tetrafluoropropionic acid (2b). HFPO (16.6 g, 0.1 mol) was introduced gradually with stirring into a mixture of trifluoroethanol (19.3 g, 0.19 mol), KOH (19 g, 0.34 mol), water (40 mL), ether (50 mL), and Bu₄NBr (1.5 g), maintaining the temperature of the reaction mixture <30 °C. Then the mixture was stirred for 1 h more at ~20 °C, and 30% HCl was added to acidic pH. The ethereal layer was separated and dried with MgSO₄, and the fraction with b.p. 82–92 °C (35 Torr) was isolated by distillation. The repeated distillation gave 16 g of compound **2b**, b.p. 61–63 °C (10 Torr), 68% yield (based on HFPO taken in the reaction) (*cf.* Ref. 3: b.p. 125–127 °C). ¹F NMR, δ : –3.3 (3 F(1)); 4.0 (3 F(3)); 54.5 (1 F(2).

2-Phenoxytetrafluoropropionic acid (2c) was obtained analogously from HFPO and phenol in 40% yield, b.p. 93–98 °C (3 Torr). ¹F NMR, δ : 5.2 (3 F); 42.5 (1 F). Without further purification acid **2c** was transformed into potassium salt **1c**, pyrolysis of which is described below.

Ethyl trifluorovinyl ether (3a) was synthesized by the pyrolysis of potassium salt **1a** in 10% yield; b.p. and the ¹F NMR spectrum coincide with the published values⁹ (acid **2a** was synthesized by the earlier described method⁵).

2,2,2-Trifluoroethyltrifluorovinyl ether (3b). A solution of acid **2b** (16 g, 0.065 mol) in MeOH was neutralized with a solution of KOH in MeOH (using phenolphthalein as indicator) and evaporated *in vacuo*, and the residue was dried over P_2O_5 at 110 °C (2–3 Torr), divided, and mixed with dry sand (20 g), and subjected to pyrolysis at 10–15 Torr heating with a burner (or in the bath with Wood's alloy at 225–280 °C). Volatiles were collected in a trap (–78 °C), and the condensate was distilled to obtain ether **3b** (8.5 g, 67%), b.p. 41–44 °C (b.p. and the ¹F NMR spectrum are identical to the described values^{3,10}).

Phenyl trifluorovinyl ether (3c). A mixture of potassium salt **1c** (10.4 g, 0.037 mol) (the salt was pre-dried over P_2O_5 at 110–115 °C and 3 Torr) and dry sand (13 g) was subjected to thermolysis in an oily pump vacuum, collecting the pyrolyzate in a trap (-78 °C). The distillation of the condensate gave ether **3c** (5.9 g, 63%), b.p. 132–134 °C (b.p. and the ¹F NMR spectrum are identical to the described values^{11,12}).

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