NMR ANALYSIS IN THE TECHNOLOGY OF PERFLUORO(VINYLOXY)BUTANOIC ACID ESTER PRODUCTION

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Abstract: Spectrum characteristics of fluorine compounds at all stages of perfluoro(vinyloxy)butanoic acid methyl ester synthesis, including fluorosulfatizing mixture obtainment and hexafluoropropylene oxidation stage were described and clarified. Mixtures in various ratios were analyzed. Approaches for reactive compounds recording and methodology for quantitative evaluation of mixture content on each manufacturing stage were described.

Keywords: nuclear magnetic resonance, NMR fluorine-19, perfluorinated compounds, hexafluoropropylene oxide, fluorosulfatizing mixture, membranes' monomers.

Introduction

Electrochemical ion-exchange membranes are applied almost across the board – from a technology for caustic soda production up to lithium batteries in mobile phones. Fluorine compounds, for example, perfluoro-4-(vinyloxy) butanoic acid methyl ester, which is produced on the base of the Federal State Unitary Enterprise "Russian Scientific Center" Applied Chemistry", can be used as a monomer for such membranes. The steps for a monomer preparing operate with compounds having high corrosive activity, which excluded the usage of traditional chromatographic analysis procedure. The simplest experiment NMR – recording of a panoramic spectrum with resonant lines integration, allowed to establish structure of nearly all obtained compounds, either of the main reactions, or of side reactions. The qualitative and the quantitative content of the products were controlled by ^{19}F NMR.

Mixtures were analyzed on Bruker WP80SY 80 MHz spectrometer. Chemical shifts in ^{19}F spectra were taken in ppm from CFCl$_3$ using hexafluorobenzene (-162.90 ppm) as a standard. Signals of solvents are taken as standards in H^{1}NMR spectra (δ, ppm, from TMS): 2.05 - acetone-D$_6$; 2.50 - DMSO-D$_6$, 7.26 - CDCl$_3$.

While conducting the quantitative NMR analysis of sulphonyl fluorides in a mixture with starting compounds and admixtures, which are formed either during the electrochemical

fluorination, or electrolysis, it is necessary to integrate each particular signal or signal group [1, 2]. Next, to sum the obtained data $\Sigma(I)=I_1+I_2+\ldots+I_n$. Integrated area of the resonance line I_a is found separately, a is the quantity of fluorine atoms that gave it, n is the total quantity of atoms, which gave a signal, in the determined molecule. Molar content is found according to the formula

$$W = \frac{n\left(\frac{I_a}{a}\right)}{\overset{\circ}{a} \ I_n}$$

. Chemical shifts, which are used as analytical, on the further schemes are marked with

«*». «Analytical» groups signals allow to assume the presence of a compound in a mixture and «compile a molecule» by integral intensities of other parts. Standard statistic processing of results was held: abnormality check, belonging to normal distribution; allowable discrepancy determination between parallel definitions, random component error boarders, maximum systematic inaccuracy.
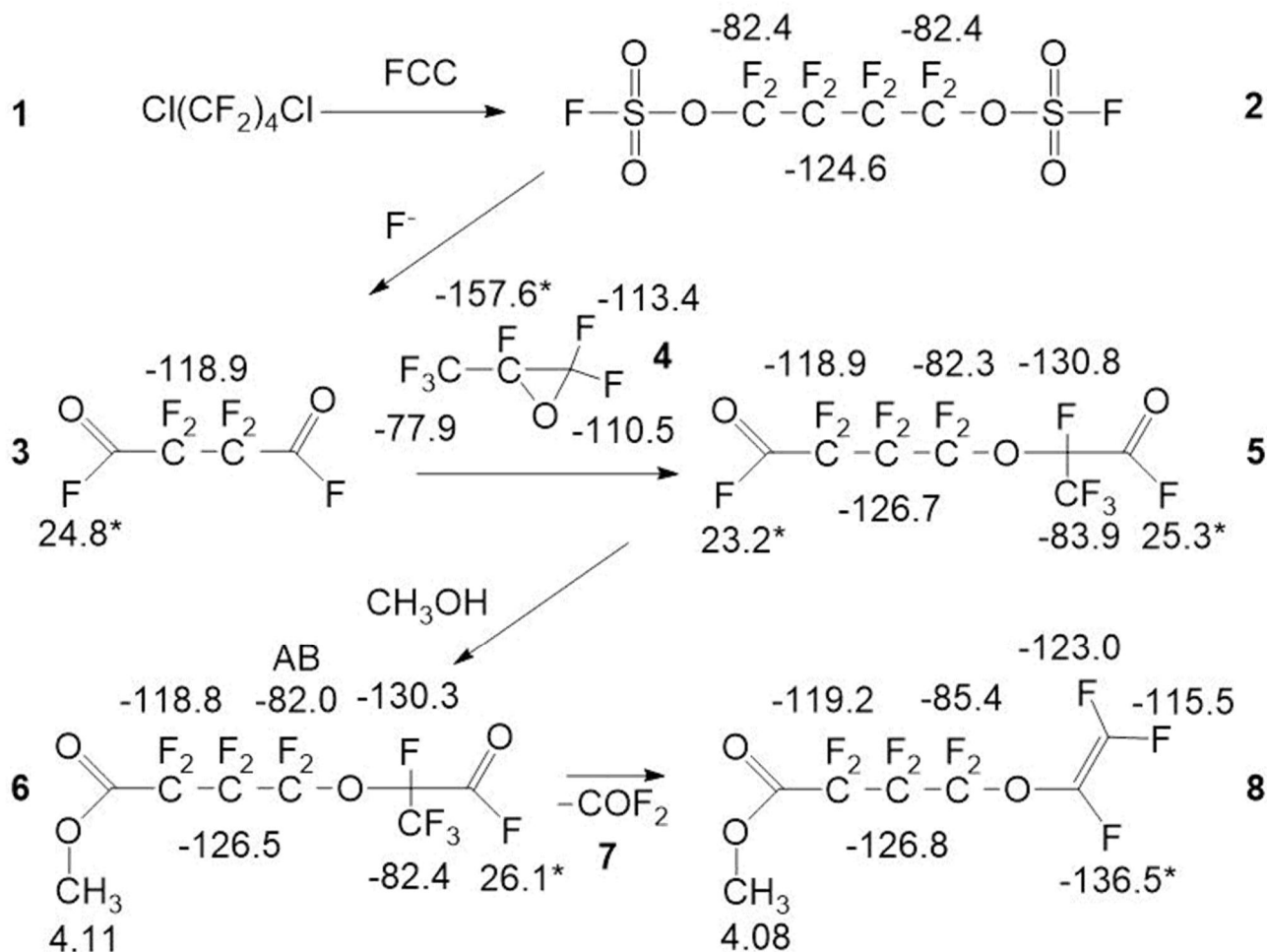
Literature review

Perfluorinated vinyl esters have been used as co-monomers for formation of curing sites in fluorinated polymers and as monomers for producing fluorine-containing polymers with special functions, such as fluoroelastomer and cation-exchange groups, in a membrane with selective permeability in the production of chlorine and caustic soda. Methods of synthesizing perfluorinated vinyl esters having an ester group are disclozed in patents [3,4]. The general methods include the following laborious reactions: (1) esterification of perfluorodiacyl fluoride and hexafluoropropylene oxide to give perfluoro (2-methyl-3-oxaalkane) diacylfluorides on cesium fluoride (2) solvolysis and synthesis of dimetal salt and (3) thermal synthesis decomposition and esterification to produce the desired product with a relatively low yield .

An easy and efficient synthesis for perfluorinated vinyl esters having ester group is described in the article by Yamabe with colleagues by pyrolysis of asymmetrical diacyl fluoride having FC(O)–CF(CF$_3$)–O– group on one end and FC(O)–CF$_2$– group – on the other end, at the temperature of about 290–370°C in gaseous phase without loss of –COF group[5].
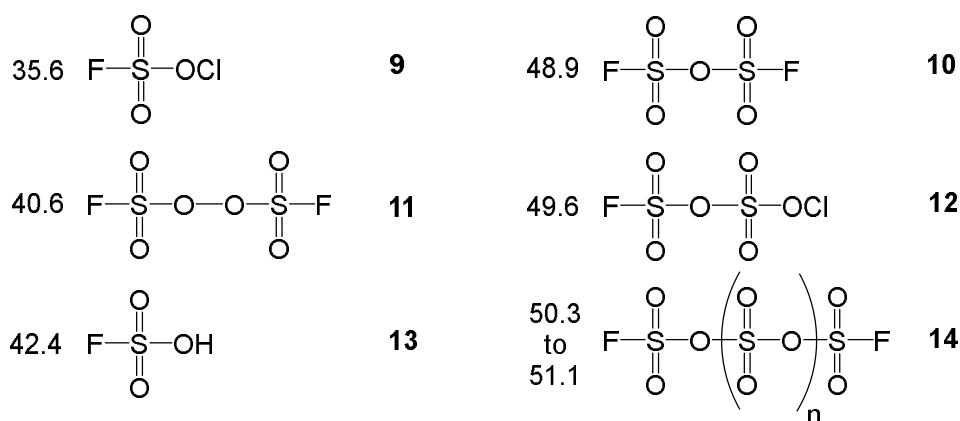
Results and Discussion

The scheme for the preparation of the monomer and the spectral characteristics of the compounds, obtained during the synthesis steps, are shown in the picture 1. Compound **5** is prepared by known method using potassium fluoride followed by pyrolysis [6]. Depending on the composition of the mixture, the chemical shifts of the initial halocarbon-318 lie in the region of -68 ppm (-CF $_2$CF $_2$Cl) and -119 ppm (-CF$_2$CF$_2$Cl); formed carbonyl difluoride COF$_2$ -19 -22 ppm. Analysis time 25 -30 min, the total error of the determination of the major component does not

exceed 3%. For the spectra of the AB type, the chemical shift of the center of the line is given.

1 $Cl(CF_2)_4Cl$ $\xrightarrow{FCC}$ **2**
(sulfonic fluoroanhydride $F-S(O)_2-O-CF_2-CF_2-CF_2-CF_2-O-S(O)_2-F$; shifts -82.4, -82.4, -124.6)

F^-

4 $F_3C-C(F)(-O-)(CF_2)$ (shifts -157.6^*, -113.4, -77.9, -110.5)

3 $O=C(F)-CF_2-CF_2-C(=O)F$ (shifts -118.9; 24.8^*)

5 $O=C(F)-CF_2-CF_2-CF_2-O-C(CF_3)(F)-C(=O)F$ (shifts -118.9, -82.3, -130.8, -126.7, 23.2^*, -83.9, 25.3^*)

CH_3OH

6 AB $O=C(OCH_3)-CF_2-CF_2-CF_2-O-C(CF_3)(F)-C(=O)F$ (shifts -118.8, -82.0, -130.3, -126.5, -82.4, 26.1^*; CH_3 4.11)

$-COF_2$ → **7**

8 $O=C(OCH_3)-CF_2-CF_2-CF_2-O-C(F)=C(F)F$ (shifts -119.2, -85.4, -123.0, -115.5, -126.8, -136.5^*; CH_3 4.08)

Picture 1. Scheme for monomer obtainment and spectral characteristics of the formed compounds.
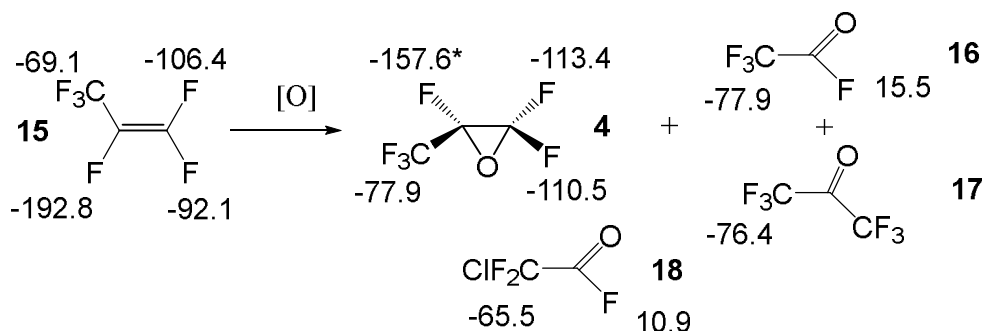
The first step for the production of a monomer is the preparation of a fluorosulfating mixture (FCC) based on sulfonic acid fluoroanhydrides [7, 8]. NMR method for fluorosulfate mixture analysis was chosen because the given mixture has high reactive and corrosive activity, so the possibility of chromatographic analysis is nearly excluded. Analysis by NMR includes spectra recording of 0,5 ml of a mixture in a 5 mm fluoroplastic ampoule with an inner capillary with deuteroacetone or deuterodimethylsulfoxide with additive component - hexafluorobenzene as a standard. A single-use of standard glass ampoules is possible. The fluorosulfate mixture analysis time is 30-40 min., ultimate total error of basic components definition does not exceed 2 % re.

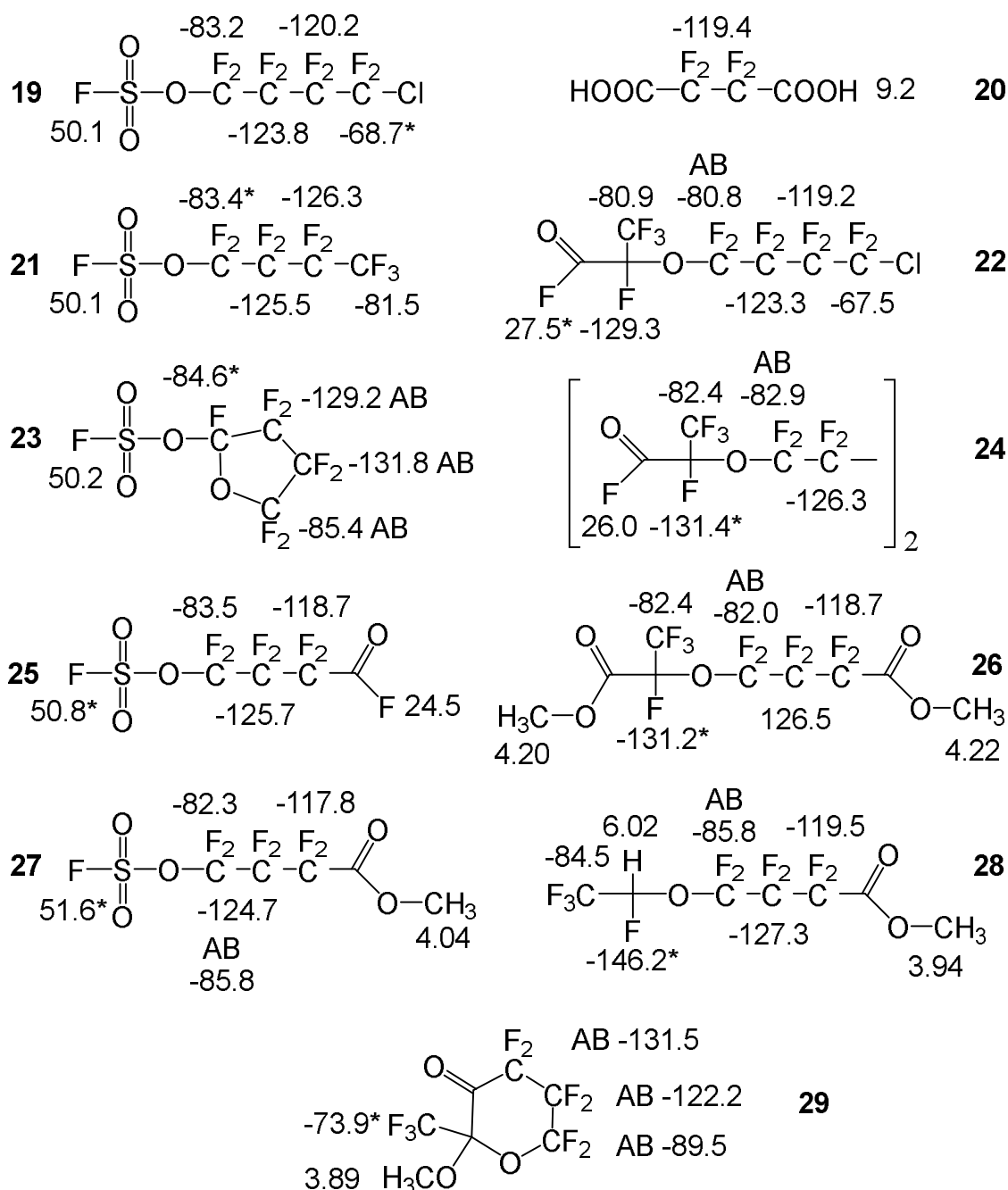*Picture 2. Spectrum characteristics of fluorosulfate liquid.*

Spectrum characteristics of fluorosulfate mixture components, such as chlorine fluorosulfat, chlorine fluoropyrosulphate, di(fluorosulfuryl)oxide, di(fluorosulfuryl)peroxide, fluorosulfonic acid, are shown in the picture 2.

NMR spectra of hexafluoropropylene oxide and the found admixtures are worth to describe separately [9]. Fluorine C$\underline{F}$-CF$_3$ chemical shift is used as analytical. Fluorine NMR signals position in hehafluoropropylene oxide strongly depends on a mixture content and may vary 157,6±3 ppm. Used methodology of NMR analysis for technological hexafluoropropylene oxide includes bubbling of gaseous products of hexafluoropropylene oxidation through 1 ml of deuterochloroform with addition of standard hexafluorobenzene in a glass ampoule (5 mm) during 2-2,5 min. with a speed 120-180 ml/min. Accurate quantification of the 2,2,3-trifluoro-3-(trifluoromethyl)oxirane obtained becomes complicated not only because of physical and chemical characteristics of investigated products, but also due to the missing data for solubility of hexafluoropropylene oxide and admixtures in deuterated solvents. Spectrum characteristics of the found products are shown in the picture 3. Chlorinated derivative **11** was found as an admixture, and it was probably formed during sample preparation for analysis.

Picture 3. Spectrum characteristics of hexafluoropropylene oxide and found admixtures.

In the picture 4 there are shown spectrum characteristics of the range of byproducts, which were found during the elaboration of the technology.

Picture 4. Spectrum characteristics of admixtures, which were found during the target monomer synthesis stages.

Conclusion

The NMR method can be used not only to establish the structure of the resulting compounds, but also as as a reference method at deviation of the process of synthesis of the methyl ester of perfluorovinyloxybutanoic acid from the preset process parameters. The publication describes methods of quantitative determination of the composition of highly reactive fluorine-containing compounds.

We have described the spectral characteristics and the procedure for the quantitative analysis of

the following compounds: 1,4-dichloroperfluorobutane 1, 1,4-bis-fluorosulfonyloxyperfluorobutane - **2**, succinic acid difluoride **3**, hexafluoropropylene oxide **4**, 4-(3-oxoperfluoropropane-2-yl)oxy-perfluorobutanoic acid fluoride **5** and it's methyl ester **6**, carbonyldifluoride **7**, perfluorio-4-(vinyloxy)butanoic acid methyl ester **8**, chlorine fluorosulfate **9**, oxydisulfurylfluoride **10**, bis-sulfurylfluoride peroxide **11**, chlorine fluoropyrosulphate **12**, fluorosulphonic acid **13**, polysulfuric acids difluorides **14**, hexafluoropropylene **15**, trifluoroacetyl fluoride **16**, hexafluoroacetone **17**, difluorochloroacetyl fluoride **18**, 4-chloro-1-fluorosulfonylperfluorobutane **19**, perfluoroamber acid **20**, 1-fluorosulfonyloxyperfluorobutane **21**, 4-chloro-1-fluorosulfonyloxy-perfluorobutane **22**, 2-fluorosulfonylperfluorofuran **23**, 1,4-bis((3-oxopropane-2-yl)oxy)perfluorobutane **24**, 4-fluorosulfonylperfluorobutanoic acid fluoride **25**, 4-(3-methoxy-3-oxoperfluoropropane-2-yl)oxy-perfluorobutanoic acid methyl ester **26**, 4-fluorosulfonylperfluorobutanoic acid methyl ester **27**, 4-(1-hydroperfluoropropane -2-yl)oxy-perfluorobutanoic acid methyl ester **28**, 2-methoxy-2-(trifluoromethyl)dihydro-2H-perfluoropyran-3(4H)-one **29**.

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