

Study of the process of synthesis of perfluorosulfo fluoride and its derivatives

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Introduction

Electrochemical fluorination (ECF) is a method of fluorine introduction into an organic or inorganic substrate by means of electrode reaction. It is known [1] that only by the ECF method it is possible to obtain a number of perfluorinated organic compounds with preservation of a functional group or a structure of an initial compound containing a heteroatom in the molecule.

Among a big number of perfluorinated compounds produced by the ECF method the most attractive for industry are some amines, ethers and derivatives of fluoroanhydrides of carbonic acids and sulfo-acids. At present a great interest is shown in fluorine-containing sulfur-containing organic compounds as perspective fluorinating agents, raw materials for electrolytes of chemical current sources, raw materials for synthesis of new fluorine-containing organic compounds.

Perfluoroethylsulfo fluoride (PFESF) and its derivatives belong to such compounds.

This paper presents the results of investigation of the synthesis of perfluoroethylsulfo fluoride, perfluoroethylsulfo-acid and barium salt of perfluoroethylsulfo-acid. Ethylsulfo fluoride and ethylsulfo chloride were used as raw materials for the ECF.

Experimental method

The synthesis of ethylsulfo fluoride was made by replacement of a chlorine atom with fluorine in a medium of anhydrous hydrogen fluoride over catalyst. The process was carried out in a hermetically sealed reactor filled up to 75% with catalyst; the reactor was fed with a mixture of hydrogen fluoride and ethylsulfo chloride. The reaction was carried out at heating and under regulated pressure. After the reaction completion, hydrogen chloride generating during the reaction course was removed by CaO in such a way that the pressure in the system did not exceed a desired value, the desired product (ethylsulfo fluoride) was poured out into a vessel prepared.

The electrochemical fluorination was carried out in an electrolyzer of Simons type with an inside airlift made of carbon steel. The electrolyzer was equipped with a counterflow cooler for condensation and return into the electrolyte of hydrogen fluoride carrying away with electrolysis gases. A coil with circulating water was placed into the electrolyzer for cooling the electrolyte.

The electrode pack consisted of alternating anode and cathode nickel plates. The current load in the experiments was changing and was from 2.5 to 15 A. The current density in all cases was different also and was changed from 0.005 to 0.03 A/cm² accordingly.

The synthesis was carried out by electrolysis of the following solution: 10-20 wt% of ethylsulfochloride (ESC) and 10-20% and 10-20 % of ethylsulfofluoride (ESF) + 0.1 wt.% of sodium fluoride in liquid anhydrous hydrogen fluoride. The electrolysis was made either with periodical dozing (1-2 times per hour) or up to completion.

The raw PFESF evolved from the electrolyzer together with electrolysis gases was condensed in a receiver cooled to temperature of minus (50-75)^oC.

It has been ascertained that perfluoroethylsulfofluoride is dissolved in liquid anhydrous hydrogen fluoride in considerable amounts/ With the purpose to purify perfluoroethylsulfofluoride dissolved from hydrogen fluoride the raw was passed through water and then through 100% sulfuric acid or silica gel for drying.

The raw material in such a way separated from hydrogen fluoride and dried was forwarded to rectification where the desired product of 99.0-99.7% purity was isolated. The product was analyzed by gas-liquid chromatography (GLC). The GLC analysis was made on a Russian "Tsvet-100" instrument equipped with a heat conductivity detector and a column filled with silochrom-80 with 20% ~~0.1~~ trisbetacyanacetophenone.

Barium salt of perfluoroethylsulfofluoride was obtained by hydrolysis of perfluoroethylsulfofluoride in a hermetically sealed steel reactor at permanent mixing. This process was controlled by such parameters as temperature, pressure and pH of the solution. The temperature was within 80^oC. The pressure and pH were parameters for control of the process completion. After the process completion (pH=7, P=0) the solution was filtered, BaF₂ precipitated was separated and the solution prepared was evaporated to produce a salt which was then dried to the water content of 0.1% in it.

The process of distillation of perfluoroethansulfo-acid from under 100% sulfuric acid was carried out in glassware. Mixing was continuously made in the reactor. Perfluoroethansulfo-acid was synthesized from its barium salt and 100% sulfuric acid.

Experimental results and their discussion.

As it is known the ECF process runs much better if in the molecule of the raw material is even one fluorine atom. That is why we studied the ECF process comparing the parameters of ECF of ethylsulfo chloride and ethylsulfo fluoride. For this study we have developed a technology for making ethansulfofluoride, a raw material for electrochemical synthesis of perfluoroethylsulfofluoride.

It has been found that the current yield of perfluoroethylsulfofluoride (PFESF) in the electrochemical fluorination of ethylsulfofluoride (ESF) reaches 65%, whereas in the case of ethylsulfochloride the yield was 36% maximum and depended on the amount of electricity passed through the electrolyte. In the beginning of the experiment the current yields were

relatively high and they reduced with time. The electrode surface was covered with a film of unknown content that made difficulties in the ECF process. The literature data have confirmed that. For example in publications of N.Ignatiev et al. [2] the ECF of ethyl sulfochloride gave 16% yield, whereas the yield in the case of ethylsulfofluoride reached 82%. The content of the desired product in the raw material also is higher in the ECF of ethylsulfofluoride (95%) in comparison with ECF of ethylsulfochloride (43-49%). Besides perfluoroethylsulfofluoride

the anodic gas always contained admixtures of the following compounds: $\text{CF}_3\text{SO}_2\text{F}$, CF_4 , C_2F_6 , SO_2F_2 , fluorine monoxide F_2O . Hydrogen was the cathode reaction product.

The raw material of perfluorosulfofluoride had the following content:

CF_4 , C_2F_6 ~ 16%

SO_2F_2 , $\text{CF}_3\text{SO}_2\text{F}$ ~ 12%

$\text{C}_2\text{F}_5\text{SO}_2\text{F}$ ~ 60-65%

Non-identified admixtures ~ 7-12% (probably subfluorinated products) The data of electrochemical fluorination of ethyl sulfochloride (ESC) and ESF are given in the following table.

Table. Data of the electrochemical fluorination of ethanesulfonyl chloride and fluoride

Initial compound	Anodic current density A/cm ²	Voltage V	Q Ah/ Ah/L	Raw produced, g	η , % of raw	PFESF Content in raw, GLC %
ESC	0,005 - 0,03	4 - 7,5	1145,5/1678	258	up to 36	43 - 49
ESF	0,005 - 0,03	4,8 - 6,0	579,5/878	211	up to 65	up to 95

A study of the effect of electrolytic additives and duration of the electrolyte continuous work on the ECF process also has been carried out. It was found that an addition of NaF as a conductive substance increased considerably the duration of the electrolyte continuous work. The data obtained do not co-ordinate with the data of paper [3] which found that an addition of NaF negatively influenced the yield of the desired product.

After the raw rectification the desired product of PFESF was isolated with a purity of 99.7%. The isolated perfluoroethylsulfofluoride was used for development of a method to synthesize perfluoroethylsulfo acid via its barium salt.

The main parameters of the present processes were determined and it was shown that the water content in the barium salt played an extremely important role because during conversion of this salt to perfluoroethylsulfo acid by means of 100% sulfuric acid in the presence of water there were formed monohydrates of this acid. That makes considerable difficulties in isolation of the pure desired acid. The yield in the stages of synthesis of the salt and acid was 93-98%. The perfluoroethylsulfo acid was isolated after vacuum distillation with the content of the main substance of 99% minimum.

The study in this direction has been continued.

References

1. J. Simons " Fluorine and its compounds", Publishing house of foreign literature. Moscow,1956
2. N.Ignat'ev, A. Kucherina and P.Sartori , Acta Chemica Scandinavica 53 (1999) 1110-1116
3. Cauguis G., Keita B., Pierra G., Jaccaud M., J.Electronal. Chem., 100 (1979) 205-215

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