

Received: January, 2012

About the mechanism of electrochemical synthesis of perfluoroalkylbromide

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Abstract: Measurements of the electrode polarization and the preparative electrolysis evidenced that perfluoroalkyl bromide can be obtained by the electrolysis of perfluorocarboxylic acids in water-acetonitrile medium containing sodium bromide on the platinum anode due to the electrochemical desorption of the adsorbed bromine atoms during the discharge of the perfluoroalkyl carboxylic anion.

Keywords: perfluoroalkylbromide, perfluorocarboxylic acids, synthesis Kolbe, bromine, acetonitrile, radiopaque substance, flame arresters, polarizing researches, preparative electrosynthesis, electrochemical desorption, platinum-anode.

Perfluorocarbons containing bromine atoms are effective flame arresters. They have been used to protect personnel and valuable electronic equipment if the ignition occurs in a confined space [1]. Because of the lability of the bromine atom both in radical and ionic reactions it is possible to use its perfluoroalkyl compounds in the synthesis of new organofluorine compounds. Perftoroktilbromid has been used as a radiopaque component in gas transfer liquids in medicine [2].

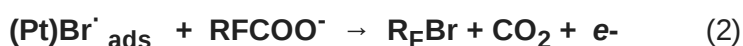
A number of chemical methods have been represented for producing substances that require stringent conditions and the use of complex equipment. These substances do not provide sufficient purity and reproducibility of the title product properties [3].

The Kolbe electrosynthesis has been successfully used for the synthesis of different perfluorochemicals [4-6]. This method does not require high temperatures and pressures, and provides good reproducibility under mild conditions of electrolysis.

It is known that elektrochemical version of Hunsdiecker-Borodin reaction with the formation of corresponding perfluoro alkyl halogenide is carried out by the electrolysis of solutions of partially neutralized perfluorocarboxylic acids and halogens in the medium of a mixture of acetonitrile-water (1:1) [7]. The use of perfluorononane acid in the presence of elemental bromine on a platinum anode at a current density of 0.01-0.03 A/cm² allowed to obtain perfluoroalkyl bromide in 94% yield. [8].

In the presence of elemental chlorine a wave of halogen oxidation appears in the polarization curve on platinum. The wave is at least 1 volt previous to the adsorption and discharge of perfluoroalkyl carboxylic anion. It has been suggested that the adsorption of halogen and the discharge of anions fluorocarbon acids occur at different parts of the anode surface with different power characteristics.

Anode condensation of perfluoroalkyl radical with the bromine radical on the platinum anode apparently occurs according to the mechanism of electrochemical desorption:



Sufficiently low rate of the process is limited by the low concentration of bromine free radicals. The process is accompanied by a substantial yield of Kolbe dimer due to the adsorption of perfluoroalkyl

The electrolyte was prepared by mixing 3.09 g (0.03 mole) of sodium bromide and 4.64 g (0.01 mol) of perfluoropelargonic acid with 50% vol. solution of acetonitrile in water. The volume of electrolyte was adjusted to 20 mL. The electrolyte was separated into two layers: a lower aqueous layer was a solution of sodium bromide, which salted out perfluoropelargonic acid dissolving in the upper layer of acetonitrile.

When mixing the layers the emulsion was formed. The electrolysis was carried out with cooling water at 25 ° C, anode current density - 0.3 A/cm², current strength - 1.32 A until the exhaustion of perfluoropelargonic acid, when the electrolyte in an hour became neutral and homogenized. Bromine liberated on the anode slightly stained the electrolyte. After carrying out of the electrolysis at the bottom there was a liquid product in the form of a heavy organofluoric layer which was separated, washed with 5% Na₂CO₃, dried over MgSO₄ and rectified.

4.40 g of the liquid product was isolated. Boiling point = 143 °C. By NMR spectra of ¹⁹F (Table 1) the product was identified as perfluoro-1-bromooctane (the main substance content was 97% by mass). The admixture (3%) is perfluorohexadecane as the product of the Kolbe synthesis. The yield of perfluoro-1-bromooctane was 91% mole by substance and 37% by current.

Preparative synthesis of perfluoro-2-bromo-2 ,5-dimethyl-3,6-dioxanonane.

20 ml of similarly prepared mixture of 4.96 g (0.01 mole) of perfluoro-2 ,5-dimethyl-3 ,6-*dioxanonanoic* acid and 3.09 g of NaBr (1,5 gmol/l) was added to 50% solution of acetonitrile and water in the electrolyzer. The electrolysis was carried out with stirring at 25 °C, the current strength - 0.88 A. The anode current density was reduced to 0.2 A/cm². After an induction period of 1 hour formation of the product was observed, this dripped from the anode surface to the bottom of the electrolyzer forming the third lowest layer.

After 40 minutes of the electrolysis, the electrolyte became neutral and two top layers were homogenized. The fluoroorganic lower layer was separated and treated similarly as described above. The yield was 5.3 g of almost pure title perfluoro-2-bromo-2 ,5-dimethyl- 3,6-dioksanonane identified in accordance with the NMR spectra of ¹⁹F shown in Table 1. Boiling point = 139 °C at 740 mm Hg. The dimerization product content according to the Kolbe synthesis did not exceed 1% by weight. The yield of perfluoro-2-bromo-2 ,5-dimethyl-3,6-dioxanonan was 99 % by substance and 36% by current.

EXPERIMENTAL RESULTS AND DISCUSSION

Polarization measurements

Figure 1 shows the anodic polarization curves of platinum in water-acetonitrile 0.5 M solutions of perfluoro-2 ,5-dimethyl-3 ,6-dioxanonanic acid recorded on the phone of 1.5 M sodium bromide in various ratios of medium components.

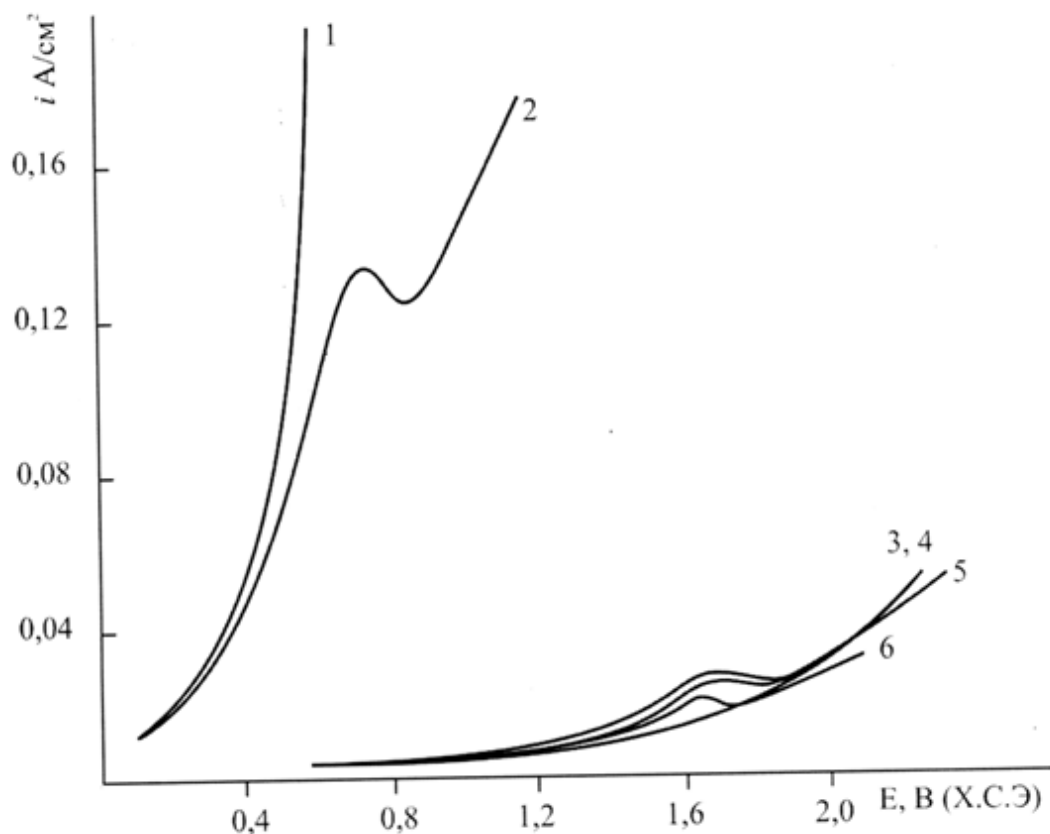


Fig. 1. Polarization curves of Pt-anode in mixtures of CN3CN: H2O on the background of 1.5 M:

1 - 30:70% by vol. 2 - 50:50% by vol., 3-6 in 0.5 M $\text{C}_3\text{F}_7\text{OCFCF}_2\text{OCFCOOH}$
solutions of CF_3 CF_3

3-30:70 3% by vol. 5 - 50:50% by vol., 4 and 6 - 90:10% by vol. 6 - in the absence of NaBr

Curves 1 and 2 were recorded in the absence of perfluorocarboxylic acid in the acetonitrile-water mixture that contained 30 and 50% by volume of acetonitrile. The curves show a rapid growth of the polarization, indicating the discharge of bromine-ions in the potential range of 0.6-0.8, and their adsorption on the anode surface. Then bromine-radicals are desorbed as dibromide-molecular.

Curves 3-5 in in the acetonitrile-water mixture that contained 30, 50 and 90 % by volume of acetonitrile show a significant increase in the polarization of the anode in the presence of perfluoro-2 ,5-dimethyl-3 ,6-dioxanonanoic acid . It was apparently associated with the displacement of water from the double-layer by anions of perfluorocarboxylic acid, subsequent discharge of the acid on the anode surface occupied by bromine radicals and the electrochemical desorption with the formation of perfluoro-2-bromo-5-methyl-3 ,6-dioxanonane.

Polarization curve 6 in the absence of sodium bromide corresponds to the electrochemical desorption of perfluorodioxalkyl radicals with the formation of dimers according to the Kolbe synthesis.

Polarization measurements at least do not contradict the possibility of discharge of the anions of perfluorocarboxylic acids on the anode surface covered by adsorbed bromine radicals.

Thus, the adsorption of a halogen radical competing with the adsorption of perfluorocarboxylic radicals and perfluoroalkyl radicals prevents the electrochemical desorption of perfluoroalkyl radicals in the Kolbe synthesis.

Preparative electrolysis

As shown earlier [5,6] the optimal yield of perfluoropolyethers under anodic condensation of perfluorooxaalkylcarbon acids in the Kolbe synthesis is obtained with volume ratio $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ as

To implement the above-mentioned competing process leading to the electrosynthesis of perfluoroalkylbromide as the title product, it was necessary to find optimal conditions for preparative electrolysis, i. e. to provide the increase in adsorbed halogen concentration on the anode and the reduction of adsorption of perfluoroalkyl carboxylate radicals on the anode.

We investigated the dependence of the perfluoroalkylbromide yield on the current density and the composition of water-acetonitrile mixtures in preparative electrolysis (0.5 M solution of perfluorohexanoic acid and perfluoro-2,5-dimethyl-3,6-dioxanonanoic acids) in the presence of 1.5 M sodium bromide on the platinum anode with the nickel cathode. The results are shown in Table 2.

Obviously, the maximum perfluoroacyl bromide yields were obtained with ratio of acetonitrile and water significantly different from the optimal implementation of the Koble synthesis 90:10. In this case, the optimum is close to an equal volume ratio 50:50, providing perfluoroalkylbromide yields above 90 mol %, whereas the yields of dimerization products in the Kolbe synthesis did not exceed 10 mol %.

The increase of the volume fraction of acetonitrile in the medium above 50% vol. causes 1) the increase of the solubility of perfluorocarboxylic acids in the mixture and 2) the adsorption of their anions on the anode during high anodic polarization, providing their Kolbe electrosynthesis with the growth of dimers yield at 90 volume % CH₃CN [5,6].

The *comparison* of the dependence of perfluoro-2-bromo-5-methyl-3,6-dioxanonane yields (by substance and by current) on the current density and medium composition with polarization measurements apparently confirm the idea that the limiting stage of the process is the adsorption of bromine radicals formed as a result of bromine anion discharge at significantly lower anodic potentials.

The reduction of acetonitrile content in the medium below 40 % by volume causes the decrease of solubility of perfluorocarboxylic acids in the mixture accompanied by micelle formation. It causes strong foaming of the electrolyte that is connected with adsorption of acid-anions that are emulgators in this case on the border electrolyte - electrolyte gases.

Salting-out effect of sodium bromide causes the formation of an emulsion with the formation of micellar structures containing acetonitrile and perfluorocarboxylic acid, stabilized on the border of the micelles with an aqueous solution of sodium bromide by anions of perfluorocarboxylic acids.

The data in Table 2 show that perfluoroalkyl bromides yield in the electrolysis performed in perfluoro-2,5-dimethyl-3,6-dioxanonane acid is much higher and less dependent on acetonitrile-water ratio than in the case with perfluorononane acid. It is likely to be associated with the difficulties in adsorption of a perfluorocarboxylate radical due to the presence of trifluoromethyl group in α -position to the carboxyl group. Free rotation of the perfluoroalkyl fragments around ester bond formation is likely to affect. It provides a more dense packing of perfluoroalkyl fragment during the adsorption process at the interface.

Conclusions

1. Preparative electrolysis of solutions of perfluorocarboxylic acids on the Pt-anode on 1.5 M sodium bromide as a phone in the medium of acetonitrile- water mixture indicates the possibility of electrosynthesis of various perfluoroalkylbromides with the substance yield of 90 mol %.

2. Polarization curves recorded on the Pt-anode in the medium of acetonitrile- water mixture in the presence of 1.5 M sodium bromide as a phone are more likely to confirm confirms the mechanism of electrochemical desorption of perfluoroalkylbromides as a result of the anion discharge of perfluorocarboxylic acids on the anode surface occupied by adsorbed bromine radicals.

Table 1. NMR spectra of ¹⁹F of perfluoroalkylbromides.

The structure of compound	Number of the signal	ϕ_{CFCl_3} ppm	The structure of the peak	The intensity of the signal	$J_{F^*-F^*}, Hz$
Perfluoro-1-bromo-n-octane ${}^1F \setminus \left[{}^5 \right]$ $BrCC^6F_2CF_2CF_2C^4F_2C^7F_2C^3F_3$ ${}^2F /$	1	-61,1	d.t.	1	$J_{F_{1-2}} 180;$
	2	-63,2	d.t.	1	$J_{F_{2-1}} 180;$
	3	-83,4	t.	3	$J_{F_{3-2}} 9;$
	4	-123,5	m.	2	$J_{F_{4-3}} 9;$
	5	-124,3	b.s.	4	
	6	-127,1	t.	2	$J_{F_{6-5}} 9;$
	7	-128,4	s.	2	
Perfluor-2-bromide--5-methyl-3,6-dioxanonan ${}^5F \setminus F^8 \quad {}^2F \setminus F^6$ $C^7F_3C^1FBrOCC^{10}FOCC^9F_2C^3F_3$ $\setminus C^4F_3$	1	71,6	m.	1	
	2	72,5	d.m.	1	$J_{F_{1-5}} 148$
	3	79,9	bs.	3	
	4	80,9	bs.	3	
	5	81,2	d.m.	1	$J_{F_{4-7}} 151$
	6	82,5	d.m.	1	$J_{F_{5-1}} 148$
	7	0	bs.	3	
	8	84,5	d.d.	1	$J_{F_{7-4}} 151; J_{F_{8-10}} 18$
	9	-127,0	s.	2	
	10	-142,2	d.	1	$J_{F_{10-8}} 18$

Table 2. Dependence of product yields on medium composition, current density and the structure of perfluorocarboxylic acids in preparative electrolysis on Pt-anode of 0.5 M solution on the background of 1.5 M .

0,5 M of perfluorooctane acid on the background of 1,5 M of sodium bromide							
CH ₃ CN		H ₂ O		Current density, D _A , A/cm ²	Yield by substance, %mole		Yield C ₈ F ₁₇ Br by current%
%vol	%mole	%vol	%mole		C ₈ F ₁₇ Br	(C ₈ F ₁₇) ₂	
80	76	20	24	0,3	40,0	60,0	8,1
60	61	40	39		58,0	42,0	23
50	44	50	56	0,1	80,5	19,5	33
				0,2	87,6	12,4	36
				0,3	91,1	8,9	37
40	34	60	66		88,0	12,0	36
0,5 M perfluor-5-methyl-3,6-dioxanonanoic acid on the phone of 1,5 M of sodium bromide							
CH ₃ CN		H ₂ O		Current density, D _A , A/cm ²	Yield by substance, %mole		Yield C ₇ F ₁₇ O ₂ Br by current,%
%vol	%mole	%vol	%mole		C ₇ F ₁₇ O ₂ Br	(C ₇ F ₁₇ O ₂) ₂	
80	76	20	24	0,2	85	15	27
70	65	30	35		77	23	24
60	61	40	39		70	30	22
50	44	50	56		99	1	32

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Recommended for publication by prof. Alexandr Y. Zapevalov