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ELECTROCHEMICAL FLUORINATION OF 4-(PERFLUORO-n-BUTYL)-n-BUTANOYL CHLORIDE*

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SUMMARY

Electrochemical fluorination of 4-(perfluoro-n-butyl)-n-butanoyl chloride produces perfluorooctanoyl fluoride in higher yields than those obtained from n-octanoyl chloride, which is the usual starting material. In particular, one of the by-products of the industrial process, the cyclic perfluoroether perfluoro-2-propyl-tetrahydropyran, is not formed. Also the other by-products, except fluorocarbon perfluoro-n-heptane, are produced in lower amounts. These results are discussed and a mechanism is suggested.

INTRODUCTION

Perfluorooctanoic acid, a precursor of commercially important emulsifying agents for polymerizations, is produced industrially by the Simons process of electrochemical fluorination starting from n-octanoyl chloride. The reaction

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mixture normally contains large amounts (often more than 50% by weight) of perfluoro-2-propyl-tetrahydropyran, perfluoro-2-butyl-tetrahydrofuran and perfluoro-n-heptane [1,2,3]. Such formation of by-products, depending on either the structure of the starting material [4] or the operational conditions [5], gives poor molar yields of perfluoro-octanoyl fluoride (about 10-14%) [4] and makes necessary to find new markets for them; so, the mixture of the cyclic perfluoroethers is now used in the electronics industry [6] and for biomedical applications [7].

One way of preventing cyclic perfluoroether formation can be the use of fluorinated precursors: so, starting from 4,4-difluoro-n-octanoyl chloride [8], the ether perfluoro-2-butyl-tetrahydrofuran is not formed. It appears that cyclization does not occur when the involved carbon atoms are already fully fluorinated.

Utilizing this observation, 4-(perfluoro-n-butyl)-n-butanoyl chloride was synthesized and used experimentally as a starting material in the Simons process. The results are reported here and compared with those obtained from n-octanoyl chloride in analogous operational conditions.

EXPERIMENTAL

Materials

The reactants used in the electrochemical fluorination experiments were commercial grade HF (maximum 0.1% H_2O), technical grade n-octanoyl chloride and 4-(perfluoro-n-butyl)-n-butanoyl chloride synthesized in laboratory (>98% pure). This last compound was prepared by addition of perfluoro-n-butyl iodide to 3-butenoic acid using azobisisobutyronitrile as initiator [9] according to the procedure of Brace [10,11]:

$$n\text{-}C_4F_9I + CH_2{=}CHCH_2COOH \longrightarrow n\text{-}C_4F_9CH_2CHICH_2COOH.$$

The acid obtained, stirred with Zn powder and 20% HCl, yielded the corresponding iodine-free compound:

$$n\text{-}C_4F_9CH_2CHICH_2COOH \xrightarrow[20\%\ HCl]{Zn} n\text{-}C_4F_9C_3H_6COOH.$$

The organic substrate was heated at reflux with $SOCl_2$ in a molar ratio 1:2 for 90 minutes and the resulting acyl chloride was distilled at reduced pressure (50 mm Hg, b.p. 101-103 °C).

The reactants used in this preparation were technical grade perfluoro-n-butyl iodide and commercial grade 3-butenoic acid (97% pure).

Apparatus and procedure

The electrochemical fluorination experiments were carried out using the apparatus described elsewhere [12]: a stainless steel cell (capacity 1.1 litres) surrounded by a cooling jacket and connected to a reflux condenser and a scrubbing system consisting of a water seal, aqueous KOH solution and aqueous saturated Na_2SO_3 solution. The anodic surface of the nickel electrodes was 825 cm^2.

In a typical procedure the cell, kept at 5 °C by circulation of a coolant through the jacket, was filled with HF; the electrolytic bath was dried in a nitrogen stream working at 4 volts with a current density of 12 mA/cm^2, until the current stabilized at 5 A. The organic substrate, dissolved in HF drained from the cell, was then added and the electrochemical process started, with a cell voltage of 5.5-6 volts and an initial current of 10 A (current density 12 mA/cm^2). The experiment was stopped when the current dropped under 5 A; the mixture drained from the cell was treated with excess of methanol to convert the acyl fluoride into the corresponding esters.

Analysis

Quantitative analysis of the reaction mixture was carried out on a Perkin-Elmer Sigma 3 gas chromatograph, using a stainless steel column (1m x 2mm) filled with Carbopack 0.01% SP 1000 programmed (120 °C for one minute, then 10 °C/min until 200 °C, kept for 5 minutes). Helium was used as carrier gas (flow rate 20 ml/min). Peak areas were recorded directly on a Perkin-Elmer Sigma 1 System.

Mass spectroscopy was also used to identify the main compounds of the reaction mixture by comparing their spectra with standard reference spectra.

RESULTS AND DISCUSSION

Table 1 shows the experimental conditions of the electrochemical fluorination trials carried out either with 4-(perfluoro-n-butyl)-n-butanoyl chloride (experiments 1-4) or with n-octanoyl chloride (experiments 5 and 6).

TABLE 1

Experimental data on 4-(perfluoro-n-butyl)-n-butanoyl chloride [(F-B)BC] and n-octanoyl chloride (n-OC) electrochemical fluorination.

	Experiment	Acyl chloride (g)	Acyl chloride (moles)	Volts	mA/cm^2 (initial)	Amp-h passed / Amp-h theor.	Time (h)	Reaction mixture (g)	Reaction mixture (F-OF*)°	F-OF* molar yield (%)
(F-B)BC	1	242	0.74	5.6÷6.0	12.1	0.879	26	225	39.3	28.8
	2	236	0.73	5.7÷6.0	12.0	0.861	25	215	39.6	28.0
	3	248	0.76	5.6÷6.1	12.1	0.878	27	229	40.3	29.2
	4	240	0.74	5.5÷6.1	12.1	0.871	26	225	39.0	28.5
n-OC	5	121	0.74	5.6÷5.9	12.1	0.875	77	260	15.6	13.2
	6	117	0.72	5.6÷6.0	12.0	0.870	75	251	14.9	12.5

*F-OF = perfluoro-octanoyl fluoride isomers.

° GLC weight percentages.

The GLC percentages and the molar yields reported here are for the perfluoro-octanoyl fluoride as normally formed in the industrial production of perfluoro-octanoic acid (a mixture of the linear compound and two other isomers not yet identified, named here ISO-I and ISO-II).

Table 2 shows the corresponding composition by weight of the original reaction mixtures calculated from data obtained by GLC analysis of the esterified mixtures, using the pure identified components as internal standards. The following empirical formula was used to calculate the reported values:

$$(\%)_2 = \frac{(\%)_1 \cdot W_1 \cdot M_2}{W_2 \cdot M_1},$$

where: $(\%)_1$ = GLC percentage in the esterified mixture;

$(\%)_2$ = corresponding percentage in the original mixture;

W_2 = calculated weight of the original mixture corresponding to the weight W_1 of the esterified mixture;

M_2 and M_1 = molecular weight of the compound in the original and in the esterified mixture respectively.

Figure 1 compares the mean compositions of the electrochemically fluorinated mixtures for the tested compounds.

From the examination of these data it can be noted that starting from 4-(perfluoro-n-butyl)-n-butanoyl chloride:

- perfluoro-2-propyl-tetrahydropyran is not formed;
- perfluoro-2-butyl-tetrahydrofuran is also formed in small yield;
- the perfluoro-octanoyl fluoride isomer ISO-I is not formed;
- the total amount of fluorocarbons (perfluoro-n-heptane + cyclic perfluoroethers) slightly decreases from 57.5% to 44.5%;
- the amount of the other unidentified by-products decreases;
- the molar yield of perfluoro-octanoyl fluoride increases from 12.8% to 28.6%;
- no tar was found either in the electrolytic bath or on the electrode surface;
- the electrochemical process has a shorter operational time: the current

TABLE 2

Composition of the reaction mixtures in the electrochemical fluorination of 4-(perfluoro-n-butyl)-n-butanoyl chloride [(F-B)BC] and n-octanoyl chloride (n-OC).

	Experiment	n-C_7F_{15}COF (F-n-OF)	ISO-I(°)	ISO-II(°)	FP*	FF*	n-C_7F_{16}	Others	Tar
(F-B)BC	1	37.8	-	1.5	-	14.9	29.3	16.5	no
	2	38.3	-	1.3	-	15.6	28.9	15.9	no
	3	39.1	-	1.2	-	14.8	29.8	15.1	no
	4	37.4	-	1.6	-	15.1	29.5	16.4	no
n-OC	5	12.7	1.7	1.2	11.8	27.9	18.1	26.6	yes
	6	11.1	2.1	1.7	12.2	27.1	18.7	27.1	yes

(°) ISO-I, ISO-II } = unidentified perfluoro-octanoyl fluoride isomers.

*FP = perfluoro-2-propyl-tetrahydropyran

*FF = perfluoro-2-butyl-tetrahydrofuran.

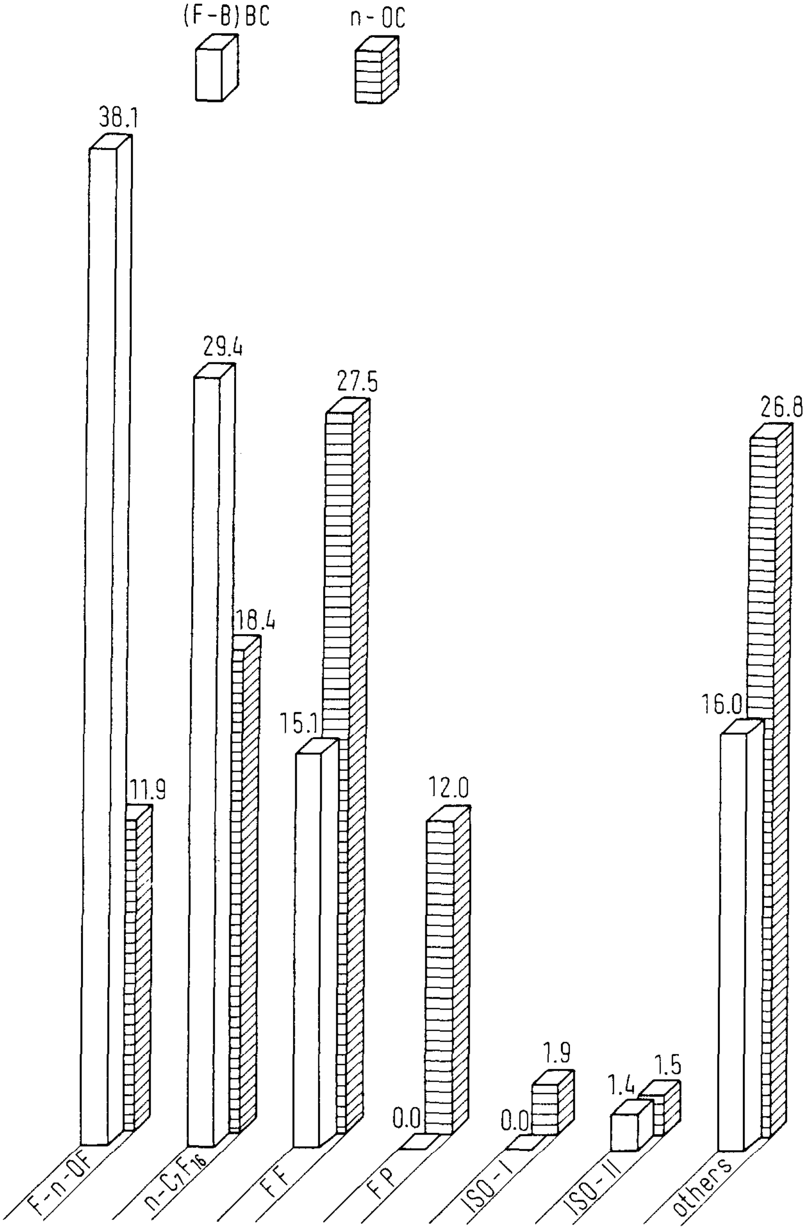


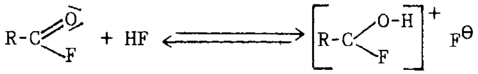
Fig. 1. Mean wt % of the components in the reaction mixtures yielding from EC fluorination of 4-(F-n-butyl)-n-butanoyl chloride [(F-B)BC] and n-octanoyl chloride (n-OC).

consumption is lower and the production rate increases from 3.4 to 8.6 grams of perfluorinated mixture per hour;

- an unexpected increase of the amount of perfluoro-n-heptane was observed.

Figure 2 shows the mean molar yields for cyclic perfluoroethers and for perfluoro-n-heptane in the electrochemical fluorination of n-octanoyl and 4-(perfluoro-n-butyl)-n-butanoyl chlorides. The absence of perfluoro-2-propyl-tetrahydropyran in the case of 4-(perfluoro-n-butyl)-n-butanoyl chloride confirms that cyclizations do not occur with $-CF_2-$ groups, and that they may arise from an interaction of a carbonyl group with a C-H bond.

As the carbonyl group is mainly in the protonated form of the equilibrium:



$$R{-}C(=O)F + HF \rightleftharpoons \left[R{-}C(O{-}H)F\right]^{+} F^{\ominus} \qquad (1)$$

cyclization could occur by one of the mechanisms reported in Figure 3 (example given for the pyran cycle). The first, using an EC_bEC_N mechanism, suggests that cyclization occurs when a radical forms on the carbon atom concerned. According to the second, cyclization arises from the high acidity of the hydrogen atom in the -CHF- group. Both mechanisms exclude the possibility that cyclization occurs before fluorination of the molecule has began.

In the electrochemical fluorination of 4-(perfluoro-n-butyl)-n-butanoyl chloride, because of the impossibility of having a radical or an acidic hydrogen atom at position 5, perfluoro-2-propyl-tetrahydropyran does not form. Moreover, as fluorination (according to EC_bEC_N mechanism) starts from carbon atom 4, this latter is quickly fluorinated in the early step of the process and soon prevented from cyclization. Thus, perfluoro-2-butyl-tetrahydrofuran forms in a smaller amount than with n-octanoyl chloride.

The formation of perfluoro-n-heptane evidently occurs with COF_2 loss (this compound is found in the off-gases). This loss may occur in a perfluoro-n-octanoyl fluoride molecule at the moment that it becames fully fluorinated. At this point, equilibrium (1) is shifted to the non-protonated form, because the inductive effect of the R_F- group reduces the availability of the oxygen lone pairs. The carbonyl group can then undergo an oxidation with radical formation:

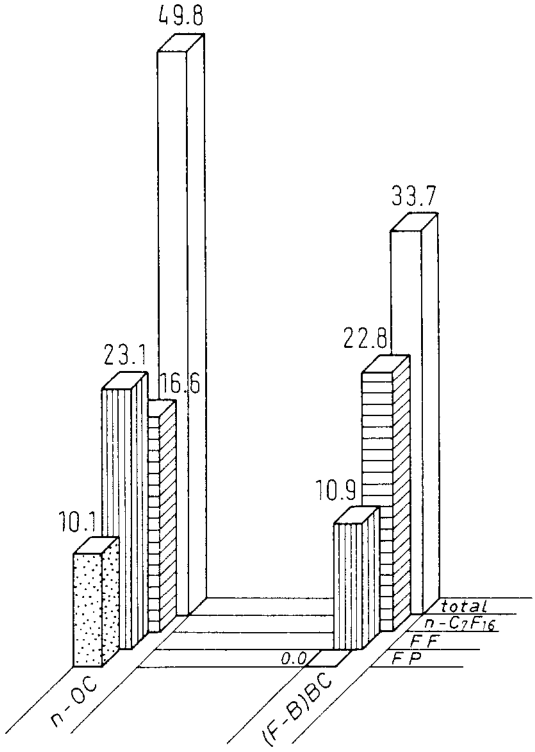
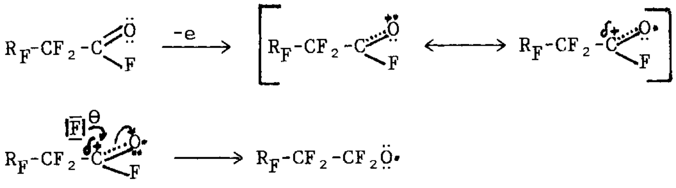


Fig. 2. Mean molar yields for FF, FP and n-C_7F_{16} in the EC fluorination of n-octanoyl chloride (n-OC) and 4-(F-n-butyl)-n-butanoyl chloride [(F-B)BC].



Perfluoro-n-heptane is formed from this radical by COF_2 loss:

$$C_6F_{13}\text{-}CF_2\text{-}CF_2O\bullet \xrightarrow{-COF_2} C_6F_{13}\text{-}CF_2^{\bullet} \xrightarrow[+\,F^{\ominus}]{-e} C_7F_{16}.$$

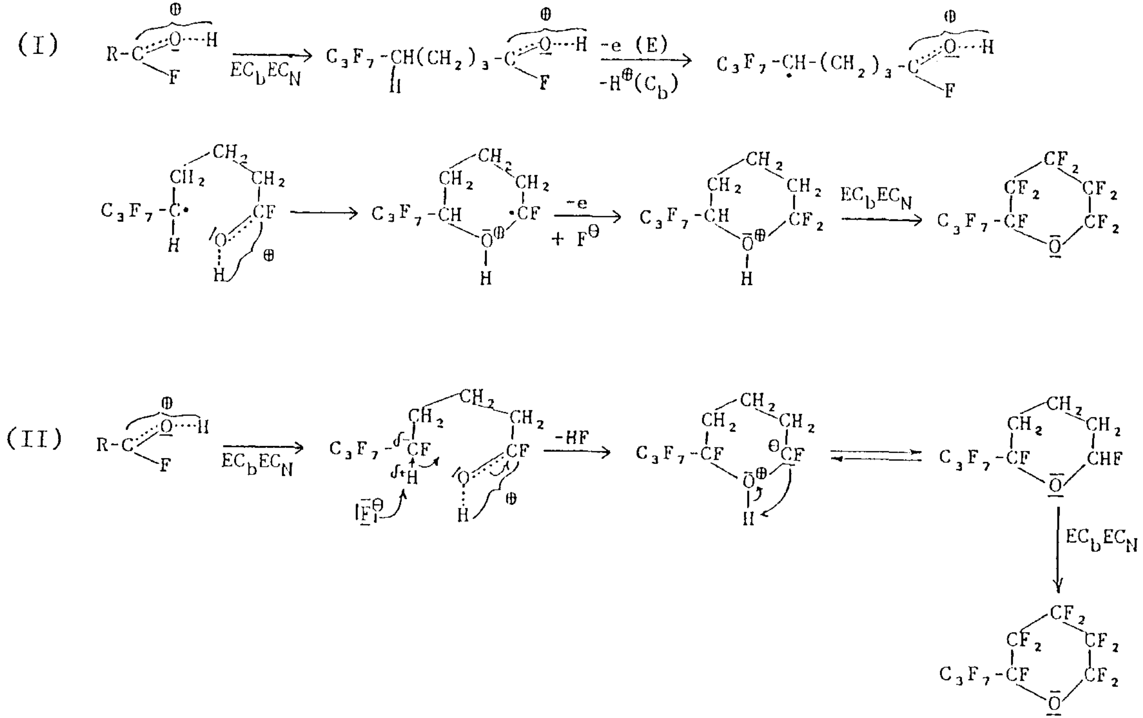


Fig. 3. Suggested mechanisms for cyclic perfluoroethers formation.

This mechanism agrees with the larger amounts of perfluoro-n-heptane found in the fluorination of 4-(perfluoro-n-butyl)-n-butanoyl chloride than n-octanoyl chloride fluorination. This can be explained if one considers that in this latter case, because of a greater extent of cyclizations, the molecules retaining their linear form until their complete fluorination are less numerous than the cyclic ones; then, perfluoro-n-heptane forms in a smaller amount than cyclic perfluoroethers (see Fig. 2). In the case of 4-(perfluoro-n-butyl)-n-butanoyl chloride cyclization is much reduced, a larger number of molecules retains their linear form and perfluoro-n-heptane is formed in a larger amount than cyclic perfluoroethers.

Finally, fewer by-products are formed and less tar occurs, probably because:

- the electrochemical process for 4-(perfluoro-n-butyl)-n-butanoyl chloride is shorter; and
- due to the partially fluorinated precursor, only the hydrogenated portion of the molecule can undergo secondary decomposition reactions.

CONCLUSIONS

The use of fluorinated precursors prevents cyclic perfluoroether formation in the Simons process for the electrolytic production of perfluoro-octanoic acid. Thus, employing 4-(perfluoro-n-butyl)-n-butanoyl chloride it is possible to avoid perfluoro-2-propyl-tetrahydropyran formation; although there is a larger amount of by-product perfluoro-n-heptane, the molar yield of perfluoro-octanoyl fluoride and its weight percentage in the reaction mixture increase. Furthermore, the electrochemical process is shorter and does not yield tar or degradation products.

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