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Yield improvement in the electrochemical production of perfluoro-octanoic acid*

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Abstract

The possibility of obtaining real yield improvements in the industrial electrochemical production of perfluoro-octanoic acid is discussed on the basis of recent experimental data obtained using perfluorohexyl acetyl chloride in place of octanoyl chloride as a starting material. In particular, the effect of the non-formation of cyclic by-products on the yield of perfluoro-octanoic acid has been examined, as well as considering previous results obtained starting from a different partially fluorinated precursor, 4-perfluorobutyl butanoyl chloride. The yield of perfluoro-octanoic acid from perfluorohexyl acetyl chloride was less than expected, because of an accompanying increase in perfluoro-n-heptane formation.

Introduction

Perfluoro-octanoic acid is a well known precursor of important emulsifying agents for industrial polymerizations. At present its industrial production is accomplished by the Simons method [2, 3] consisting of the electrochemical fluorination in anhydrous hydrogen fluoride of n-octanoyl chloride to perfluoro-n-octanoyl fluoride, as the precursor of perfluoro-octanoic acid. Besides the desired reaction product, large amounts of by-products are usually found in the reaction mixture, including either straight-chain or cyclic perfluorinated compounds (Fig. 1). For this reason, perfluoro-n-octanoyl fluoride is generally obtained in only 15%–20% molar yield [4].

As can be seen from Fig. 1, cyclic perfluoroethers are the most significant by-products, consisting of a mixture of perfluoro-2-alkyl-oxolanes and perfluoro-2-alkyl-oxanes, with the generally observed mean composition also reported in Fig. 1 [5]. The formation of these cyclic by-products appeared to provide an important investigative tool in attempts to improve the yield of the electrochemical process. An increase in yield of perfluoro-n-octanoyl fluoride should result if these by-products are not formed.

The possibility of avoiding the formation of cyclic perfluoroethers in the electrochemical process has been confirmed by several authors [6–8] who started from straight-chain structures in which certain positions of the molecule were already fluorinated. In particular, $CF_3CH_2CH_2COCl$ and n-$C_4F_9C_3H_6COCl$ were used in place of the corresponding alkanoyl chlorides and the results seemed to offer interesting opportunities for an increase in yield of the desired perfluoroacyl fluoride.

To confirm the above results n-$C_6F_{13}CH_2COCl$ was synthesized and used as the starting material in the electrochemical fluorination process for the preparation of perfluoro-n-octanoyl fluoride. The experimental results are reported in the present work and the possibility of increasing the yield of the desired product is discussed.

Experimental

n-Perfluorohexyl acetyl chloride, $C_6F_{13}CH_2COCl$, was prepared from the corresponding acid, which in turn was synthesized from perfluoro-n-hexyl iodide and vinyl acetate [9] using the well-known AIBN-catalyzed radical addition [10–13]. Electrochemical fluorination was carried out using an iron industrial cell (capacity of 25 l) charged with 25 kg of anhydrous hydrogen fluoride and 900 g (2.37 mol) of n-$C_6F_{13}CH_2COF$. The following experimental conditions were employed: initial concentration of solute, 3.47% w/w; anodic surface area

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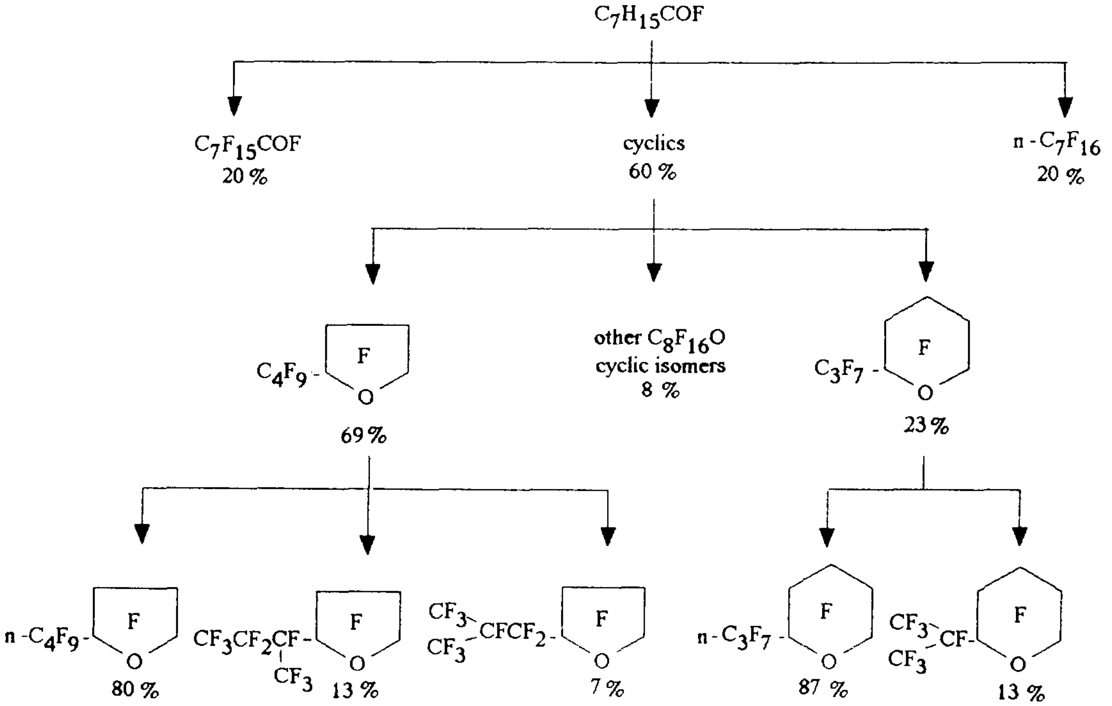

Fig. 1. Mean % w/w composition of the reaction mixture obtained in the industrial electrochemical fluorination of n-octanoyl fluoride.

of the nickel electrodes, 1.12 m^2; cell voltage, 5–6.5 V; initial current, 10 A; and current density, 9 A m^{-2}.

Excess hydrogen fluoride was removed from the reaction mixture by evaporation and subsequent treatment with NaF. Quantitative analysis of the residue was carried out on a Perkin-Elmer Sigma 3 gas chromatograph (1 m×2 mm stainless-steel column filled with Carbopack 0.01% SP 1000, temperature programmed with He as the gas carrier) and a Perkin-Elmer Sigma 1 system.

Product identity was confirmed using a Carlo Erba model MFC 500/QMD 1000 GC–MS spectrometer (30 m×0.5 mm capillary fused silica column packed with PS 264, temperature programmed with He as the gas carrier) and by means of a Bruker AC 200 NMR spectrometer.

Results and discussion

The experimental results for the electrochemical fluorination of n-$C_6F_{13}CH_2COCl$ are summarized in Table 1 and compared with those obtained with different starting materials. As a general comment on these data, it seems evident that on using a partially fluorinated starting material the formation of cyclic perfluoroethers is reduced or even avoided. These results can be explained by considering the intramolecular cyclization mechanism of the original straight-chain structures.

TABLE 1. Mean composition (% w/w) of the reaction mixtures obtained from the electrochemical fluorination of different substrates R–COCl

R group	Acyl fluoride	*F*-Heptane	*F*-Oxolane	*F*-Oxanes	Others
n-C_3H_7	34.0	–	24.0	–	42.0[a]
$CF_3CH_2CH_2$	60.0	–	<1.0	–	39.0[a]
n-C_7H_{15}	11.9	18.4	27.5	12.0	30.2[b]
n-$C_4F_9C_3H_6$	38.1	29.4	15.1	–	17.4[b]
n-$C_6F_{13}CH_2$	33.1	55.1	–	–	11.8[c]

[a] From ref. 7: balance values of unreported by-products.
[b] From ref. 8: homologues and isomers of main perfluorinated by-products.
[c] 8.5% of $C_7F_{15}H$ and 3.3% of C_7F_{14}.

Cyclization arises from the interaction of the carbonyl oxygen with the electrophilic carbon atom in position 4 (oxolane-ring formation) or 5 (oxane-ring formation) of the same molecule. The overall effect of such a cyclization process is a C–H bond cleavage and a C–O bond formation. Either the radical mechanism or the radical-cation (EC_bEC_N) mechanism, both of which have been suggested for the electrochemical fluorination of organic compounds in anhydrous hydrogen fluoride [1, 14–17], suggest homolytic cleavage of the C–H bond, as shown in Fig. 2. When carbon atom 4 or 5 is converted into a radical as a consequence of anodic oxidation, then intramolecular cyclization can occur as outlined

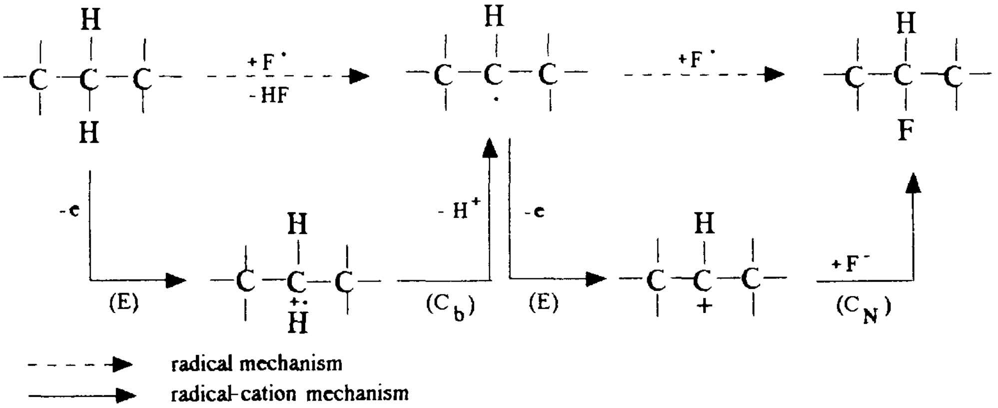

Fig. 2. Outline of the two mechanisms proposed for the Simons method for the electrochemical fluorination of organic compounds.

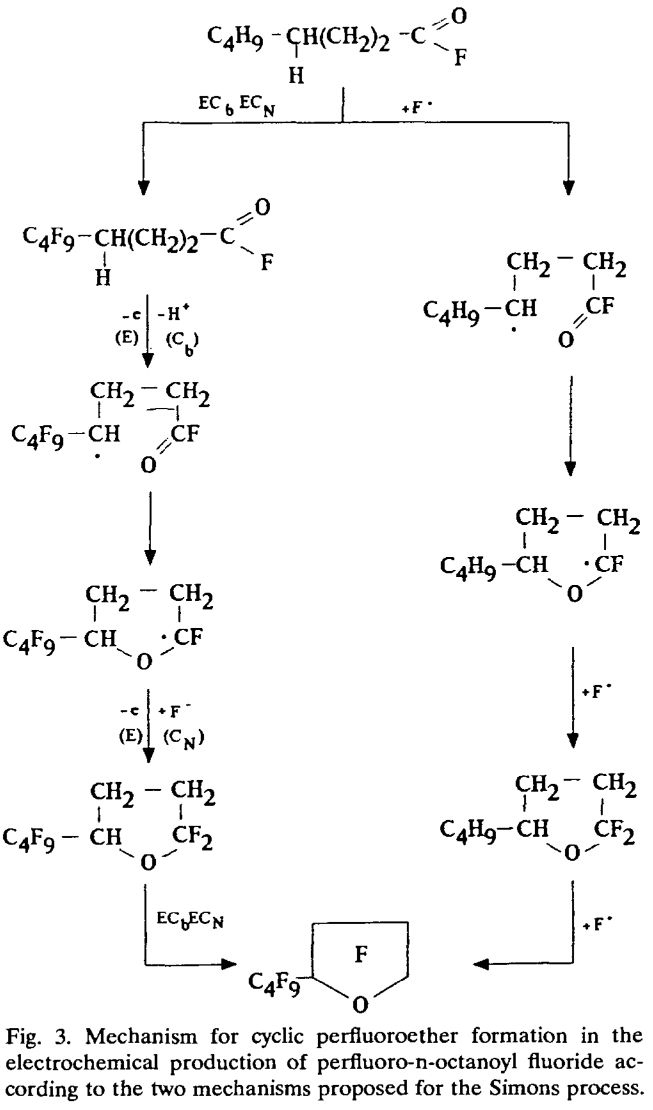

Fig. 3. Mechanism for cyclic perfluoroether formation in the electrochemical production of perfluoro-n-octanoyl fluoride according to the two mechanisms proposed for the Simons process.

in Fig. 3, where the formation of the *F*-oxolane ring is given as an example.

If carbon atom 4 or 5 of the precursor molecule is already fluorinated, the cyclization process is significantly or fully hindered due to the strength of the C—F bond. The experimental results reported in Table 1 are then clearly understandable. Hence, it is obvious why, if $CF_3CH_2CH_2COCl$ is used in place of $CH_3CH_2CH_2COCl$, as reported in ref. 7, the amount of *F*-oxolane in the final reaction mixture is reduced to less than 1% w/w and, as a consequence, the yield of the desired perfluoroacyl fluoride increases up to 60% w/w.

Similar results were obtained when partially fluorinated compounds were used in place of n-$C_7H_{15}COCl$. In previous work [8] conducted starting from $CF_3(CF_2)_3(CH_2)_3COCl$ (where carbon atom 5 is fully fluorinated), *F*-oxanes were not formed while *F*-oxolanes were present in the reaction mixture, although in an amount lower than that obtained from the corresponding fully hydrogenated molecule. The yield of the desired perfluoroacyl fluoride correspondingly increased, as did that of *F*-n-heptane. The accompanying decrease in the amounts of other by-products should also be pointed out.

In the present work, n-$C_6F_{13}CH_2COCl$ (where both carbon atoms 4 and 5 are fully fluorinated) was used as the starting material leading to the total disappearance from the reaction mixture of both cyclic perfluoroethers and a further reduction of other cyclic by-products. The amount of the desired perfluoroacyl fluoride was however less than expected from such by-product reduction, whilst a remarkable increase was found in the yield of *F*-n-heptane.

The larger amount of *F*-n-heptane relative to the decrease in the yield of cyclic by-products can be explained from the mechanism of *F*-n-heptane formation. The most likely suggestion is the loss of COF_2 from an incompletely fluorinated molecule still adsorbed on the anode, according to the mechanism outlined in Fig. 4. Thus, anodic oxidation of the carbonyl group

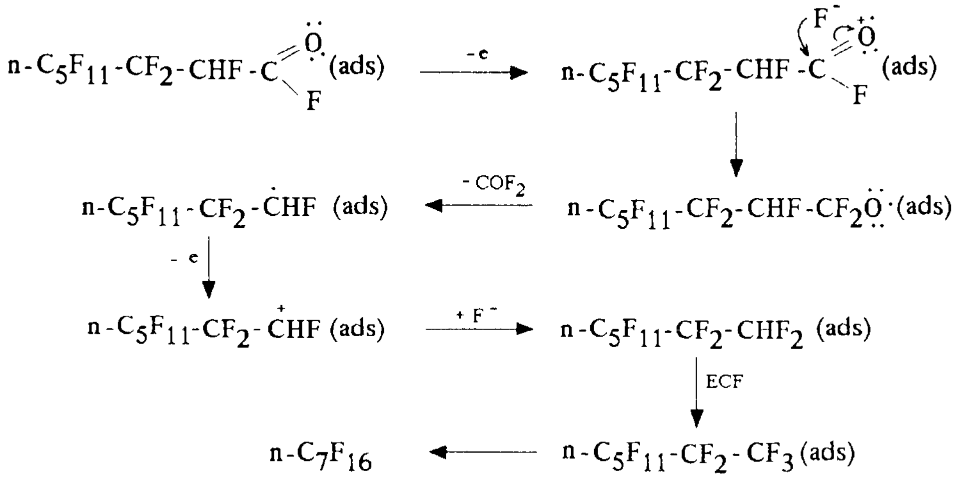

Fig. 4. Mechanism of perfluoro-n-heptane formation in the electrochemical production of perfluoro-n-octanoyl fluoride.

gives a radical-cation which reacts with a fluoride anion present in the electrolyte to give a radical which eliminates a COF_2 molecule. The new radical is rapidly oxidized on the anode to the corresponding cation, whose stabilization is effected by addition of the fluoride anion to give n-$C_7F_{15}H$. This compound undergoes further fluorination to give the final *F*-n-heptane.

This hypothesis is confirmed by the presence of appreciable amounts of n-$C_7F_{15}H$ and n-C_7F_{14} in the reaction mixture when n-$C_6F_{13}CH_2COCl$ was used as the precursor. In particular, n-C_7F_{14} is probably formed from n-$C_7F_{15}H$ during treatment of the reaction mixture following the electrochemical process.

It can be seen from Table 1 that *F*-n-heptane formation which usually occurs in the Simons process is particularly pronounced when the extent of the intramolecular cyclizations is reduced. This may be explained as due to the decreased formation of cyclic structures, with molecules which retain their linear form through to complete fluorination being more numerous. The number of molecules that can lose COF_2 and form *F*-n-heptane is thus increased.

Conclusions

The experimental results show that by an appropriate choice of starting material it is possible to avoid the formation of perfluorinated cyclic ethers, which are the most important by-products in the electrochemical production of perfluoro-octanoic acid. This however does not greatly affect the formation of the desired perfluoroacyl fluoride, owing to a greater production of perfluoro-n-heptane.

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