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Electrochemical fluorination of *N*,*N*-dimethylperfluoroacylamides

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Abstract

The electrochemical fluorination (ECF) of *N*,*N*-dimethylperfluoroacylamides gives the corresponding perfluoro-*N*,*N*-dimethylacylamides in low yield. With increase of the number of carbon atoms in the perfluoroacyl radical the yield of the required perfluoro-*N*,*N*-dimethylacylamides is slightly increased. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electrochemical fluorination; Simons process; *N*,*N*-dimethylperfluoroacylamides; Perfluoro-*N*,*N*-dimethylacylamides

1. Introduction

N,*N*-bis(trifluoromethyl)perfluoroalkanesulfonamides are convenient starting compounds for the introduction of $(CF_3)_2N$– groups into organic molecules [1,2]. These perfluorinated sulfonamides can be prepared in a one step procedure by means of the Simons process [3]. The starting materials for this process, *N*,*N*-dimethylperfluoroalkanesulfonamides, can easily be synthesized from readily available chemicals.

$$CF_3SO_2F + 2HN(CH_3)_2 \rightarrow CF_3SO_2N(CH_3) + (CH_3)_2NH_2^+F^-$$

The disadvantage of this method is the high price of trifluoromethanesulfonyl fluoride. From this point of view the application of perfluoroacyl fluorides in place of trifluoromethanesulfonyl fluoride as starting material is more reasonable.

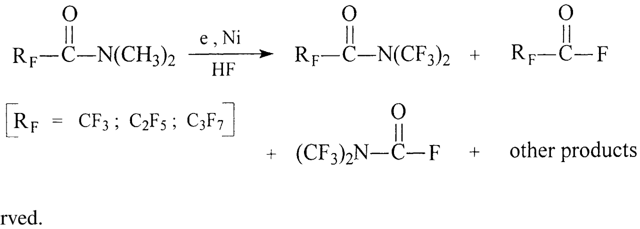
In the present study we have investigated the electrochemical fluorination (ECF) of *N*,*N*-dimethylperfluoroacylamides, which can easily be obtained from the corresponding perfluoroacyl fluorides or chlorides.

2. Results and discussion

In the literature, only one example of electrochemical fluorination (Simons process) of *N*,*N*-dimethylperfluoroacylamides, namely of *N*,*N*-dimethyltrifluoroacetamide, is given [4]. The reported yield of perfluoro-*N*,*N*-dimethylacetamide, $CF_3CON(CF_3)_2$ is very low; 48 g of this substance are obtained from 569 g of starting material, corresponding to a yield of 4.8%. Decomposition products, among them bis(trifluoromethyl)carbamyl fluoride, $(CF_3)_2NCOF$, are preferably formed.

We have repeated this experiment and also obtained a very low yield of the required perfluoro-*N*,*N*-dimethylacetamide. We believe that the low yield of perfluoro-*N*,*N*-dimethylacetamide is related to the high solubility of this product in HF which leads to its decomposition during the Simons process. We decided to investigate the ECF of homologues of *N*,*N*-dimethyltrifluoroacetamide with longer perfluorinated chains to decrease the solubility of perfluoro-*N*,*N*-dimethylacylamides in HF.

Thus, electrochemical fluorination of *N*,*N*-dimethylpentafluoropropioamide, $C_2F_5CON(CH_3)_2$ and *N*,*N*-dimethylheptafluorobutyramide, $C_3F_7CON(CH_3)_2$ was the subject of the present study.



$$R_F\!-\!\overset{O}{\overset{\|}{C}}\!-\!N(CH_3)_2 \xrightarrow[HF]{e,\,Ni} R_F\!-\!\overset{O}{\overset{\|}{C}}\!-\!N(CF_3)_2 + R_F\!-\!\overset{O}{\overset{\|}{C}}\!-\!F + (CF_3)_2N\!-\!\overset{O}{\overset{\|}{C}}\!-\!F + \text{other products}$$

$$\left[R_F = CF_3;\ C_2F_5;\ C_3F_7\right]$$

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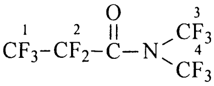
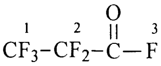
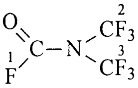
Table 1
Composition of the mixture[a] after electrochemical fluorination of $C_2F_5C(O)N(CH_3)_2$

Compound	Boiling point (°C)	^{19}F, δ (ppm)[b]	Content in the mixture (wt.%)
 $\overset{1}{C}F_3-\overset{2}{C}F_2-C(=O)-N(\overset{3}{C}F_3)(\overset{4}{C}F_3)$	49–50	-55.06 t ($6F^{3,4}$) -81.76 m ($3F^1$) -118.75 m ($2F^2$) $^5J_{F^3,F^2} = 8.0$ Hz	32.6
 $\overset{1}{C}F_3-\overset{2}{C}F_2-C(=O)-\overset{3}{F}$	-26.5 [5]	$+23.73$ tq ($1F^3$) -83.39 d ($3F^1$) -121.90 d ($2F^2$) $^4J_{F^3,F^1} = 4.5$ Hz $^3J_{F^2,F^3} = 7.7$ Hz	65.2
 $O=C(\overset{1}{F})-N(\overset{2}{C}F_3)(\overset{3}{C}F_3)$	13–15 [4,6]	$+5.38$ sp ($1F^1$) -56.47 d ($6F^{2,3}$) $^4J_{F^1,F^3} = 17.0$ Hz	2.2

[a] Trapped at −78 °C.
[b] Spectra were measured at −40 °C.

2.1. Electrochemical fluorination of $C_2F_5CON(CH_3)_2$

Ninety grams of *N*,*N*-Dimethylpentafluoropropioamide, $C_2F_5CON(CH_3)_2$, were used as starting material for the ECF process and 23.0 g of a mixture of perfluorinated products were trapped at −78 °C (see Section 3). The composition of the mixture, estimated by means of ^{19}F NMR spectroscopy, is given in Table 1. The content of perfluoro-*N*,*N*-dimethylpropioamide, $C_2F_5CON(CF_3)_2$ is still very low (non-isolated yield of 5.3%). Probably the yield can be raised due to the saturation of HF in the cell with fluorinated products if a larger amount of starting material is used for the ECF.

2.2. Electrochemical fluorination of $C_3F_7CON(CH_3)_2$

This compound was fluorinated by means of ECF under two different protocols (see Section 3). The main difference in these two experiments is the temperature and the timetable for filling of the cell with starting material. In experiment (II) the cell was re-filled with *N*,*N*-dimethylheptafluorobutyramide every 2 h to keep the Ni-electrodes active with the fluorination of starting material but not with fluorination of the desired perfluoro-*N*,*N*-dimethylbutyramide. This procedure helps to increase the contents of $C_3F_7CON(CF_3)_2$ in the resultant mixture from 10.2% in experiment (I) to 15.7% in experiment (II) (Table 2), corresponding to non-isolated yield of 7.6%. However, the main product in the reaction mixture is still perfluorobutyryl fluoride.

This is explainable by the comparatively high solubility of $C_3F_7CON(CF_3)_2$ in HF, which undergoes subsequent fluorination even in the presence of the starting material $C_3F_7CON(CH_3)_2$. That is the reason why, after every refilling of the cell with starting material, the cell voltage, which strongly decreases at the beginning of the experiment, remains practically unchanged at the end of the experiment (Fig. 1). At this point the HF in the cell is saturated with soluble materials, which keeps the conductivity of the solution the same irrespective of addition of starting material.

The presence of partially fluorinated compounds such as: $C_3F_7CON(CF_3)(CHF_2)$ and $C_3F_7CON(CHF_2)(CHF_2)$ in the reaction mixture, confirms again that ECF is a step-wise process [9].

3. Experimental details

3.1. Apparatus

A stainless-steel Simons-type cylindrical cell (total volume 360 cm^3) with an array of nickel anodes (effective anodic area: $S = 4.58$ dm^2) and cathodes with the same effective area was used for the ECF of *N*,*N*-dimethylperfluoroacylamides. The cell was equipped with a stainless-steel condenser and two FEP-traps cooled to −78 °C.

3.2. Analytical procedures

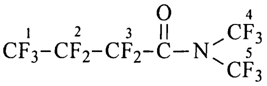
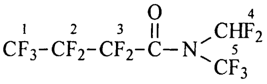
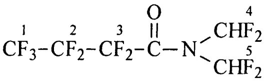
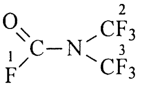
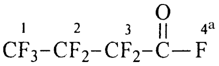
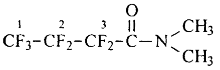
^{19}F and ^1H NMR spectra were measured for a neat liquids on the Brucker WP 80 SY spectrometer. Spectra were recorded using FEP sample tube inside a 5 mm thin walled NMR tube with an acetone-D_6 film as an external lock and CCl_3F or TMS as internal references.

Gas chromatography was undertaken with a Perkin-Elmer gas chromotograph using a column (4% OV 101 on Chromosorb GAW DMCS) of length 2.5 m and 2 mm i.d. at 40 °C. The temperature of the injector was 100 °C and the temperature of the FID detector was maintained at 250 °C. The carrier gas was He.

3.3. Chemicals

N,*N*-dimethylpentafluoropropionamide, $C_2F_5CON(CH_3)_2$, was synthesized by the interaction of pentafluoropropionyl

Table 2
Composition of the mixture after electrochemical fluorination of $C_3F_7C(O)N(CH_3)_2$

Compound	Boiling point (°C)	^{19}F, δ (ppm)	^{1}H, δ (ppm)	Contents in the mixture (wt.%), experiment	
				I	II
 $CF_3{-}CF_2{-}CF_2{-}C(O){-}N(CF_3)_2$	72–73	−54.90 t ($6F^{4,5}$) −80.18 t ($3F^{1}$) −115.75 m ($2F^{3}$) −124.57 m ($2F^{2}$) $^{4}J_{F^1,F^3} = 9.5$ Hz $^{5}J_{F^5,F^3} = 7.8$ Hz		10.2	15.7
 $CF_3{-}CF_2{-}CF_2{-}C(O){-}N(CHF_2)(CF_3)$	90–91	−54.82 m ($3F^{5}$) −80.12 t ($3F^{1}$) −99.56 dqt ($2F^{4}$) −114.30 m ($2F^{3}$) −124.79 m ($2F^{2}$) $^{4}J_{F^1,F^3} = 9.5$ Hz $^{4}J_{F^4,F^5} = 10.9$ Hz $^{5}J_{F^4,F^3} = 4.0$ Hz	7.57 t (1H) $J_{H,F} = 55.3$ Hz	6.1	4.4
 $CF_3{-}CF_2{-}CF_2{-}C(O){-}N(CHF_2)_2$	–	−80.07 t ($3F^{1}$) −99.78 dt ($4F^{4,5}$) −113.99 m ($2F^{3}$) −125.07 m ($2F^{2}$) $^{4}J_{F^1,F^3} = 9.5$ Hz $^{5}J_{F^4,F^3} = 5.0$ Hz	7.47 t (2H) $J_{H,F} = 57.02$ Hz	7.2	2.7
 $FC(O){-}N(CF_3)_2$	13–15	(Table 1)		0.7	5.3
 $CF_3{-}CF_2{-}CF_2{-}C(O){-}F$ [a]	7–9 [7]	+24.70 t ($1F^{4}$) −80.90 t ($3F^{1}$) −119.20 m ($2F^{3}$) −127.00 m ($2F^{2}$) $^{4}J_{F^1,F^3} = 8.0$ Hz		62.8	48.1
 $CF_3{-}CF_2{-}CF_2{-}C(O){-}N(CH_3)_2$ (starting material)		See Section 3		–	13.2
$CF_3CF_2CF_3$ [a]	−38 [8]	−82.30 s (6F) −131.00 s (2F)		1.3	4.0
Others				11.7	6.6

[a] ^{19}F NMR spectra were recorded at −40 °C.

fluoride (obtained in 27% yield by the ECF of propionyl chloride) with dimethylamine. 102.0 g (0.614 mol) of pentafluoropropionyl fluoride were bubbled through the stirred solution of 75.0 g (1.66 mol) of dimethylamine ("Aldrich", >99%) in 500 cm^3 of dry ether cooled in ice-water. The reaction mixture was kept overnight at room temperature, the white deposit was filtered off and washed with three portions (50 cm^3 each) of ether. The ether was distilled off and the remainder was distilled at reduced pressure. Eighty-five grams of *N*,*N*-dimethylpentafluoropropionamide (bp 98–100 °C at 18.4 kPa) [10] was obtained. Yield: 72.4%. ^{19}F NMR spectrum (solvent: acetone-D$_6$; standard: internal CCl3F), δ (ppm): −82.04 s (CF$_3$), −115.00 m (CF$_2$). ^{1}H NMR spectrum (solvent: acetone-D$_6$; standard: internal TMS), δ (ppm): 3.04 t (CH$_3$), 3.23 t (CH$_3$), $^{4}J_{H,F} = 1.0$ Hz, $^{4}J_{H,F} = 2.4$ Hz.

N,*N*-dimethylheptafluorobutyramide was prepared from heptafluorobutyryl chloride by the reaction with dimethylamine similarly. The 132.5 g (0.57 mol) of heptafluorobutyryl chloride were slowly (≈1.5 g per min) added to the stirred solution of 71.0 g (1.58 mol) of dimethylamine ("Aldrich", >99%) in 500 cm^3 of dry ether cooled in ice-water. After addition, the reaction mixture was refluxed for 1 h and left overnight at room temperature. The white deposit was filtered off and washed with three portions (50 cm^3 each) of ether. After distilling off the ether, the rest was distilled at reduced pressure to give 121.7 g of *N*,*N*-dimethylheptafluorobutyramide (bp 107 °C at 14.7 kPa) [11]. Yield: 88.6%. ^{19}F NMR spectrum (solvent: acetone-D$_6$; standard: internal CCl3F), δ (ppm): −79.51 t (CF$_3$), −111.65 m (CF$_2$), −125.04 s (CF$_2$), $^{4}J_{F,F} = 9.5$ Hz. ^{1}H NMR spectrum (solvent: acetone-D$_6$;

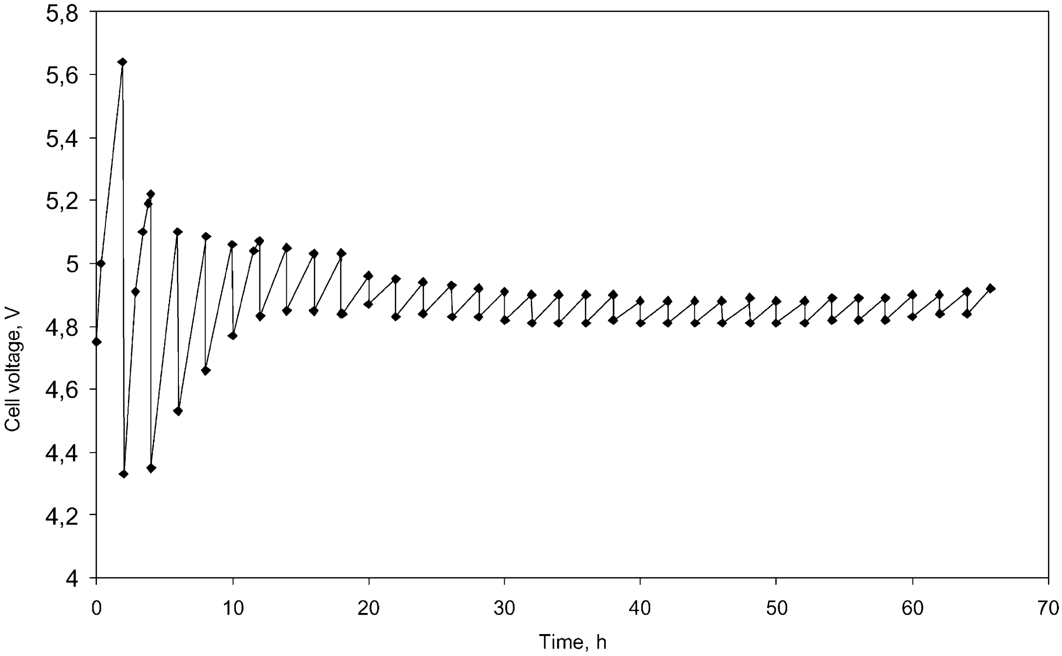


Fig. 1. Cell voltage during the ECF of $C_3F_7C(O)N(CH_3)_2$. Experiment II.

standard: internal TMS), δ (ppm): 3.06 t (CH_3), 3.23 t (CH_3), $^4J_{H,F} = 0.8$ Hz, $^4J_{H,F} = 2.4$ Hz.

3.4. Electrochemical fluorination of N,N-dimethylpentafluoropropionamide

The temperature of the cell body in this experiment was maintained at 0 °C and the temperature of the condenser was kept at −30 °C.

Ninety grams of *N*,*N*-dimethylpentafluoropropionamide was added as shown in Table 3 to 337 g of liquid hydrogen fluoride previously electrolyzed in the cell for 25 h. The gaseous products from the cell were passed through a condenser and two FEP traps at −78 °C. The electrolysis, which proceeded at a cell voltage of 4.3–5.1 V and a current density of 0.66 A/dm^2, was completed after consumption of 183.7 Ah (121.3% of the theoretical amount calculated on a 12 electron process). Twenty-three grams of a transparent liquid was obtained from the trap after separation from the HF layer.

According to ^{19}F NMR spectra this mixture contains three main substances (Table 1). By the fractional distillation perfluoro-*N*,*N*-dimethylpropioamide was isolated (3.6 g) as a pure compound; bp 49–50 °C.

Table 3

Weight of $C_2F_5CON(CH_3)_2$ (g)	Electricity consumed (Ah)
25.0	0
25.0	54.0
20.0	86.8
20.0	128.4

3.5. Electrochemical fluorination of N,N-dimethylheptafluorobutyramide

3.5.1. Experiment (I)

The temperature of the cell body in this experiment was maintained at −15 °C and the temperature of the condenser was kept at −30 °C.

The 140.4 g of *N*,*N*-dimethylheptafluorobutyramide was added as shown in the Table 4 to 338 g of liquid HF previously electrolyzed in the cell for 17 h. The gaseous products from the cell were passed through a condenser and two FEP traps at −78 °C. The electrolysis, which proceeded at a cell voltage of 4.6–5.5 V and a current density of 0.66 A/dm^2, was completed after consumption of 226.5 Ah (121.0% of the theoretical amount calculated on a 12 electron process). The 70.5 g of a transparent liquid was obtained from the trap after separation from the HF layer. This mixture was analyzed by ^{19}F NMR spectroscopy.

Dilution of the HF-solution from the cell with ice-water gave in addition 32.2 g of transparent liquid, which was dried over magnesium sulphate and analyzed by means of gas chromatography and ^{19}F NMR spectroscopy methods.

Table 4

Weight of $C_3F_7CON(CH_3)_2$ (g)	Electricity consumed (Ah)
22.4	0
27.0	30.2
22.0	73.6
27.0	102.0
22.0	141.6
20.0	175.6

The data in Table 2 show the contents of fluorinated compounds in the mixture, isolated from the trap and from the cell after ECF of *N*,*N*-dimethylheptafluorobutyramide.

By fractional distillation of the material from the trap (after warming up to room temperature 4.9 g remain) together with the product obtained from the cell, the following compounds were isolated as pure substances (for NMR data see Table 2):

1. Perfluoro-*N*,*N*-dimethylbutyramide, $C_3F_7CON(CF_3)_2$; bp 72–73 °C (isolated yield: 3.0%).
2. *N*-(trifluoromethyl)-*N*-(difluoromethyl)heptafluorobutyramide, $C_3F_7CON(CF_3)(CHF_2)$; bp 90–91 °C.

^{19}F NMR spectrum of the fraction with bp 108–115 °C shows the presence of *N*,*N*-bis(difluoromethyl)heptafluorobutyramide, $C_3F_7CON(CHF_2)_2$, as the main component in this fraction.

3.5.2. Experiment (II)

The temperature of the cell body in this experiment was maintained at 0 °C and the temperature of the condenser was kept at -30 °C.

An amount of 132.0 g of *N*,*N*-dimethylheptafluorobutyramide was added in 33 equal portions (4 g each) every 2 h to 333 g of liquid HF previously electrolyzed in the cell over 45 h. The gaseous products from the cell were passed through a condenser and two FEP traps at -78 °C. The electrolysis, which proceeded at a cell voltage of 4.3–5.6 V and a current density of 0.66 A/dm^2, was completed after consumption of 199.7 Ah (113.4% of the theoretical amount calculated on a 12 electron process). An amount of 57.1 g of a transparent liquid was obtained from the trap after separation from the HF layer. Dilution of the HF-solution from the cell with ice-water gave in addition 35.4 g of a transparent liquid, which was dried over magnesium sulphate.

Analyses of both those samples and separation of the individual compounds were carried out as in Experiment (I). Data are given in the Table 2.

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