Journal of Fluorine Chemistry, 68 (1994) 15–19

On the electrochemical fluorination of triethylamine. Part 1. Formation and properties of partially fluorinated compounds*

Anton Dimitrov[†], Stephan Rüdiger, Konrad Seppelt
Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Fabeckstr. 34–36, 14195 Berlin (Germany)

and Tatjana Peplinski
Humboldt-Universität zu Berlin, Fachbereich Chemie, Hessische Str. 1–2, 10115 Berlin (Germany)

(Received April 5, 1993; accepted September 27, 1993)

Abstract

The electrochemical fluorination (ECF) of triethylamine (TEA) has been studied with respect to changes in the composition of the anhydrous hydrogen fluoride electrolyte. Depending on the current passed, different partially fluorinated compounds have been isolated and identified during ECF. The fluorine distribution in the TEA skeleton of these compounds shows a striking similarity to the product distribution known for free-radical halogenation processes.

Introduction

The formation of partially fluorinated amines has already been reported as a part of the Simons electrochemical fluorination (ECF) process used in the preparation of perfluorinated tertiary amines [1, 2]. Among these compounds, a distinction has been drawn between intermediates yielding the crude target product (CP) and by-products: ECF leads to the consumption of both types of incompletely fluorinated amine, but only gaseous cleavage products are formed from the latter [2, 3]. Furthermore, it has been shown that all anhydrous hydrogen fluoride (AHF) soluble compounds found possess no, or virtually no, fluorine atoms bound to the carbon atoms next to nitrogen [2]. Depending on the starting material to be electrofluorinated, the concentration of such compounds can increase considerably causing the electrolyte to function 'out of control' due to their surface activity in AHF [4].

We have studied the ECF of triethylamine (TEA) (**1**), the simplest member of the family of tertiary amines having three symmetrically distributed C–C bonds, following up the fluorination process by an analysis of the AHF-soluble (HF phase) and AHF-insoluble (CP) compounds.

Results and discussion

Compounds **1–14**, summarized in Table 1, were isolated from the AHF electrolyte when ECF of **1** had been stopped after passing 30% or 70%, respectively, of the theoretically amount of current necessary for the complete fluorination of TEA. In the former case (30% is the current corresponding to a theoretical fluorine/TEA ratio of *c.* 4:1), the first droplets of CP were observed alongside the continued production of low molecular perfluorinated cleavage products (mostly CF_4 and NF_3) whose presence was already detectable at the start of ECF and whose generation continuously accompanied ECF until the latter terminated. In the second case (70% is the current corresponding to a theoretical fluorine/TEA ratio of *c.* 10:1), CP production still continued but in this case a permanent and slow increase in the voltage occurred to give the same current density. We consider this stage to be the beginning of the termination of ECF instead of the production of a steady state condition. Compounds **15–18** were identified in the CP mixture, whereas compounds **1–14** were isolated from the AHF electrolyte after distillation of the latter and an alkaline work-up procedure [1]. The quantitative distribution of compounds in the HF phase in the mixtures (see Table 1) is also shown in Fig. 1 for a sample after the passage of 70% of the current. A very similar quantitative composition for the compounds in these mixtures has been obtained using GC methods in conjunction with an FID detector rather

---

*Presented in part at the 10th European Symposium of Fluorine Chemistry, Padua (Italy), September 20–25, 1992.

[†]Author to whom correspondence should be addressed.

0022-1139/94/$07.00 © 1994 Elsevier Science S.A. All rights reserved
SSDI 0022-1139(93)02984-M

TABLE 1. Compounds isolated and identified from AHF (1–14) and from CP (13–18)[a] during the ECF of TEA

Number of F atoms	Compounds	After passage of	
		$0.3Q_{\text{theor.}}$[b]	$0.7Q_{\text{theor.}}$
0	$N(CH_2CH_3)_3$ (**1**)	+ +[c]	–
1	$CH_2FCH_2{-}N(CH_2CH_3)_2$ (**2**)	+ + +	–
2	$CHF_2CH_2{-}N(CH_2CH_3)_2$ (**3**)	+	–
	$CH_3CH_2{-}N(CH_2CH_2F)_2$ (**4**)	+ +	–
3	$CHF_2CH_2{-}N(CH_2CH_2F)(CH_2CH_3)$ (**5**)	+	+
	$N(CH_2CH_2F)_3$ (**6**)	t	–
4	$CHF_2CH_2{-}N(CH_2CH_2F)_2$ (**7**)	t	+ +
	$CH_3CH_2{-}N(CH_2CHF_2)_2$ (**8**)	t	+
5	$CH_2FCH_2{-}N(CH_2CHF_2)_2$ (**9**)	–	+ + +
6	$N(CH_2CHF_2)_3$ (**10**)	–	+ + +
	$CH_2FCH_2{-}N(CH_2CHF_2)(CH_2CF_3)$ (**11**)	–	+
7	$CF_3CH_2{-}N(CH_2CHF_2)_2$ (**12**)	–	+ +
8	$CHF_2CH_2{-}N(CH_2CF_3)_2$ (**13**)	–	+
9	$N(CH_2CF_3)_3$ (**14**)	–	t
13	$CF_3CF_2{-}N(CHFCF_3)_2$ (**15**)		
	$CF_3CH_2{-}N(CF_2CF_3)_2$ (**16**)		
14	$CF_3CFH{-}N(CF_2CF_3)_2$ (**17**)		
15	$N(CF_2CF_3)_3$ (**18**)		

[a] According to GC (FID detector), the CP consisted approximately of **18** (62%) **17** (5%), **15** (1%), **16** (1%), $CF_3{-}N(CF_2CF_3)_2$ (14%), $CF_3CF_2{-}N(CF_3)_2$ (10%), $N(CF_3)_3$ (3%), other (4%).

[b] $Q_{\text{theor.}} = 804$ A h (mol TEA)$^{-1}$.

[c] Presence in the mixture from GC analysis as relative contents: –, not detectable; t, traces; +, small amounts; + +, medium amounts; + + +, large amounts (major compounds).

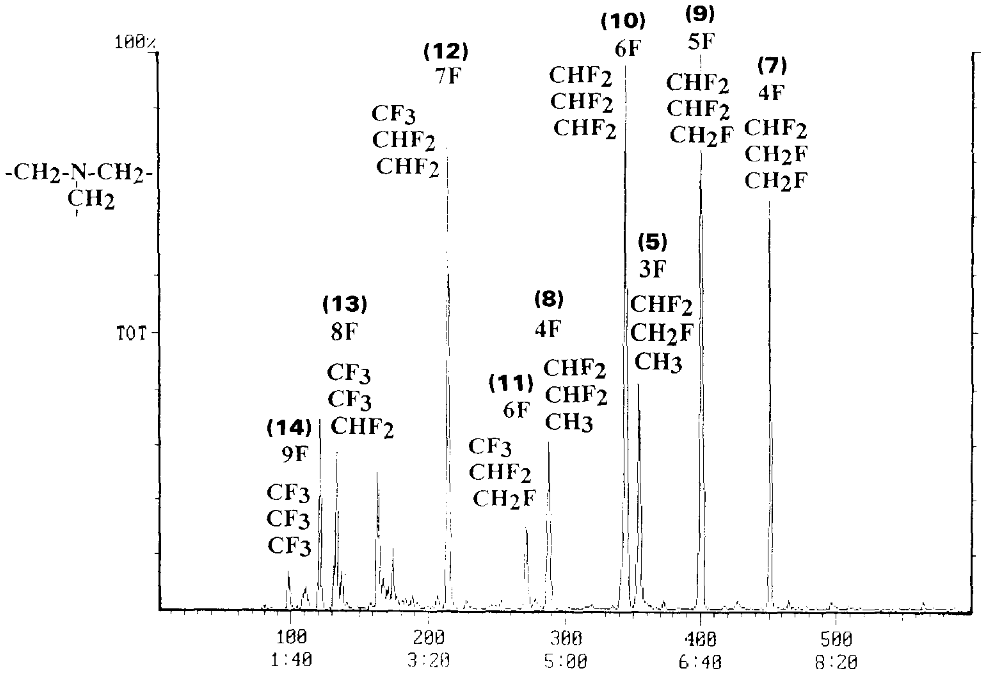
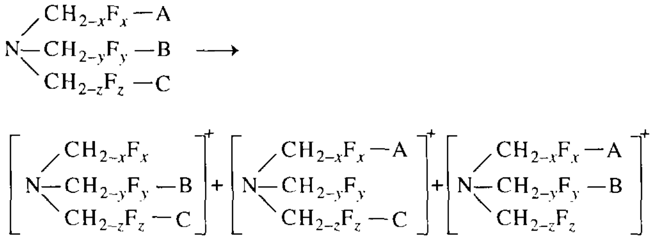


Fig. 1. Gas chromatogram of the HF phase incorporating GC/MS analysis data (sample from the ECF of TEA after 70% of the current had been passed).

than mass spectrometry. In total, the partially fluorinated compounds formed in the HF phase amounted to c. 50%–60% for $Q = 0.30Q_{\text{theor.}}$ and to 10%–20% for $Q = 0.70Q_{\text{theor.}}$, respectively, of the applied current as calculated according to ref. 1 on the basis of the total amount and the mean F content. Careful separation of the liquid CP (drained off from the bottom of the cell and also condensed from the gas stream in several traps at −78 °C) ascertained that CP formation consumed between 13%–18% at $Q = 0.30Q_{\text{theor.}}$ and between 35%–40% at $Q = 0.70Q_{\text{theor.}}$, respectively, of the applied current. The remainder of the applied current was obviously used for the formation of gaseous fluorinated fragments (e.g. CF_4, CHF_3, NF_3) but the amounts of these fragments were not determined.

Table 2 lists selected specific ions from the EI mass spectra of compounds **1** to **14**, all of which have M^+, $(M-H)^+$, $(M-F)^+$ in common as well as all the possible β-cleavage fragments but with different intensities. The possible β-cleavage fragments for the fluorinated TEA-derived compounds are:



where $x, y, z = 0, 1, 2$ and A, B, C = CH_3, CH_2F, CHF_2, CF_3. The increase in the number of fluorines in the TEA molecule leads to a decrease in the intensities of the M^+ fragments. For highly fluorinated CP compounds such as **15–18** $(M-F)^+$ occurs as the heaviest mass fragment with M^+ not being observed either in the EI or CI mode. However, β-cleavage fragments are an essential part of the mass spectra of all the compounds **1–18**. In compounds **1–14** one of these fragments also represents the base peak, providing evidence for the high order of availability of the nitrogen lone pair electrons in the stabilization of the respective ions. The formation of β-cleavage fragments follows the rule that substitution of one or two hydrogens by fluorines in the CH_3 portion of a CH_3–CH_2– radical fragment destabilizes the C–C bond, whereas substitution of all the CH_3 hydrogens stabilizes the C–C bond. In accordance with this rule, the intensities of the β-cleavage fragments decrease in the sequence: $[M-CH_2F]^+ \approx [M-CHF_2]^+ > [M-CH_3]^+ \gg [M-CF_3]^+$ (see Table 2).

The mass spectra also reveal another remarkable aspect of the fragmentation behaviour of these compounds associated with their fluorine content and fluorine distribution. Characteristic elimination of a propyl radical from the molecules causes the formation of the important fragment $[M-C_3H_{7-x}F_x]^+$, with $x = 0$–5. Again, once a CF_3 group is formed in the original TEA molecule (e.g. $=N-CH_2-CF_3$), stabilization of the C–C bonds takes place; hence, molecules with three CF_3 groups (compounds **14–18**) do not undergo propyl radical elimination, in contrast to derived TEA molecules (compounds **1–13**) with 2-fluoro- and/or 2,2-difluoro-ethyl groups. Compounds also possessing fluorinated α-carbon atoms (compounds **15–18**) exhibit the $(C_2F_5)^+$ ion as the base peak due to cleavage of the

TABLE 2. EI mass spectra of partially fluorinated TEA-derived compounds[a]

No. of F atoms	0	1	2	2	3	3	4	4	5	6	6	7	8	9
Compound fragment	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
M	24	24.2	17.6	11.8	16.3	7.8	7.5	7.5	4.2	1.5	10.5	4.1	5.6	11.8
M−H	6	4.6	2.0	2.3	2.0	1.0	2.0	1.3	1.4	0.7	0.7	0.7	–	1.2
M−F	–	–	–	–	–	–	1.3	–	3.2	5.6	3.9	7.7	8.5	3.3
$M-CH_3$	100	62.7	36.6	17.6	23.3	–	–	18.3	–	–	–	–	–	–
$M-CH_2F$	–	100	–	100	65.4	100	100	–	43.8	–	82.4	–	–	–
$M-CHF_2$	–	–	100	–	100	–	69.3	100	100	100	92.8	100	100	3.3
$M-CF_3$	–	–	–	–	–	–	–	–	–	–	26.8	16.3	47.7	100
$M-C_3H_7$	31.4	30	24.2	–	–	–	–	–	–	–	–	–	–	–
$M-C_3H_6F$	–	27.5	–	37.9	41.2	–	–	–	–	–	–	–	–	–
$M-C_3H_5F_2$	–	–	21.6	3.0	26.1	32.7	30.7	39.9	–	–	–	–	–	–
$M-C_3H_4F_3$	–	–	–	–	–	–	20.9	–	37.3	–	46.4	–	–	–
$M-C_3H_3F_4$	–	–	–	–	–	–	–	–	6.5	13.7	11.1	14.4	–	–
$M-C_3H_2F_5$	–	–	–	–	–	–	–	–	–	–	–	3.3	31.4	–
C_2H_4F	–	5.3	4.5	12.8	24.0	21.5	50.0	5.0	55.0	6.0	100	2.6	3.5	–
$C_2H_3F_2$	–	–	3.0	–	7.5	–	5.0	6.9	24.9	28.0	29.5	34.0	20.0	1.0
$C_2H_2F_3$	–	–	–	–	–	–	–	–	–	2.0	8.5	5.3	13.5	13.0

[a] Relative abundance of selected ions in percentage terms.

N−C bond in addition to β-cleavage fragments $[(M-CF_3)]^+$.

In trying to separate some individual compounds from the AHF electrolyte (Table 1), we were successful in isolating the 6F (**10**) and 7F (**12**) compounds by extraction with $CFCl_2CF_2Cl$ at a pH value between 0–4. The ^1H and ^{19}F NMR data of these compounds are listed in Table 3. Comparison of their NMR data provides evidence for the first time of a change in the fluorinated TEA molecule. Normally, an increase in the number of fluorine atoms in a molecule leads to more positive (downfield) shift of the nuclei of all the groups influenced. However, comparison of the NMR data for the 6F (**10**) and 7F (**12**) compounds shows that this is only true for the CH_2 group directly attached to the CF_3 group in compound **12**. In fact, the NMR data are not in agreement with what may be anticipated from a comparison of the CH_2CHF_2 groups in compounds **10** and **12**. Although the introduction of a seventh fluorine leads to the formation of a CF_3 group in compound **12** which has a much greater electron-withdrawing power than a CHF_2 group, the strong $-I$ effect of the CF_3 group is outweighed by the 'new quality' of the amine molecule which results in a high field shift of the H and F nuclei of the CH_2CHF_2 groups in compound **12** relative to that in compound **10**. The 'new quality' of compound **12** at this stage in the fluorination process could be due either to a flattening of the molecule (increase in the C−N−C angle) allowing charge transfer from the CF_3 group ($+M$ effect) by means of conjugation and/or hyperconjugation arising from interaction with the nitrogen lone-pair electrons or possibly the nitrogen changes its hybridization state at this particular fluorination stage.

In order to find an explanation for all these phenomena, molecular structure determinations for these compounds seem inevitable. We have already started such structural studies for the 9F compound (**14**). To date, it has not been possible to separate all the individual components of the mixtures arising from AHF (Table 1), but we are still working on this problem in an attempt to isolate and/or to synthesize more individual compounds.

TABLE 3. NMR spectra of compounds **10** and **12** (δ in ppm, J in Hz)[a]

	$N(CH_2CHF_2)_3$ (**10**)	$CF_3CH_2N(CH_2CHF_2)_2$ (**12**)
^1H NMR data		
$\delta(C\mathit{H}_2CF_3)$	–	3.31
$\delta(C\mathit{H}_2CHF_2)$	3.12	3.05
$\delta(CH_2C\mathit{H}F_2)$	5.74	5.71
^{19}F NMR data		
$\delta(CH_2C\mathit{F}_3)$	–	−71.4
$\delta(CH_2CH\mathit{F}_2)$	−120.98	−121.33
$^2J_{H,F}$	56.0	56.2
$^3J_{H,F}(CH_2CF_3)$	–	9.0
$^3J_{H,F}(CH_2CHF_2)$	14.3	14.4
$^3J_{H,H}(CH_2CHF_2)$	4.12	4.30

[a] Differences in chemical shifts were demonstrated by the simultaneous measurement of mixtures of compounds 10 and 12.

However, the results reported here are sufficient to answer the purposes of this investigation, viz. to obtain an insight into the type of fluorine distribution arising during the course of ECF substitution reactions, and to study the changes in the properties of such partially fluorinated TEA-derived compounds in relation to their fluorine content and distribution.

From the compounds identified in the AHF electrolyte and their specific fluorine distribution patterns, a free-radical process is undoubtless favoured for the ECF studied. Similar product distributions are well known for the free-radical chlorination of protonated tertiary amines, especially the substitution of the first hydrogen by chlorine proceeds principally in the nitrogen-remote carbon atom in such compounds [5]. The ECF of tertiary amines always involves N-protonated cations and we have shown recently that ECF also works well if quaternary tetraalkylammonium salts are used as the starting material [6]. Hence, the electron-withdrawing effect of the quaternary nitrogen in the protonated TEA should prevent the α-hydrogen atoms from leaving with their electrons to form HF in a free-radical fluorination process. Thus such a free-radical fluorination should give principally β-carbon fluorinated products with little, if any, α-carbon fluorinated compounds. The fact that no α-carbon fluorinated TEA isomers have been found in AHF as well as no compounds bearing a CF_3 group in addition to a CH_3 or two CH_2F groups leads to the assumption that these compounds stem from a free-radical fluorination process. Another interesting observation is that neither in the AHF electrolyte nor in the CP were compounds with 10–12 F atoms found, and the 9F compound (**14**), in which all the β-carbon atoms are completely fluorinated, was only produced in very low concentrations. Presumably, the change in physicochemical properties in going from 9F to 13F (or perfluorinated) TEA is so drastic that in the case of the 9F compound (**14**) a 'zipper mechanism' [7] applies. In order to decide whether compound **14** is a key compound in the ECF process, we are about to commence a study of the ECF of **14**.

Experimental

Electrochemical fluorinations were carried out in stainless-steel or PTFE cells as described elsewhere [1, 3]. Liquid, HF-insoluble, fluorination products (CP) were drained off and/or condensed from the gas stream

(−78 °C). The HF-soluble compounds were isolated and determined according to the method described previously [1]. Extraction with $CF_2ClCFCl_2$ was undertaken after dilution of *c.* 100 ml of the AHF electrolyte with ice/water (1:1) and stirring of the respective acid solution for 30 min with 50 ml of $CF_2ClCFCl_2$. After separation and treatment of the organic layer with $NaHCO_3$ and $MgSO_4$, the solution was filtered and the $CF_2ClCFCl_2$ distilled off. Gas chromatography was carried out on a Varian 3700 GC machine with packed columns (10% FS16 on N-AW-DMCS, 3.7 m) or on a Varian 3400 capillary GC machine (60 m column coated with DB5 silicon phase), while GC/MS analysis was undertaken with a Finnigan MAT GC/MS system 5100 GC, 50 m column with SE30; MS (quadrupole) EI, 70 eV.

NMR spectra were recorded at 300 MHz for ^1H and 282 MHz for ^{19}F on a Varian spectrometer with TMS or TFA, respectively, as external references. Values for ^{19}F are quoted relative to $CFCl_3$ [$\delta(CFCl_3) = \delta(TFA) - 78$], values upfield of $CFCl_3$ being designed as negative. Compound **18** was identified from GC, MS and ^{19}F NMR spectral analysis, while compounds **15–17** were identified by GC/MS methods and partially by their ^{19}F and ^1H NMR spectra. In MS (CI with CF_4), all compounds exhibited $(M - F)^+$ as the base peak, while in MS (EI) the fragment $(C_2F_5)^+$ served as the base peak. NMR data for $CF_3CHFN(C_2F_5)_2$ (**17**): $\delta_F - 161.8$ (d of m, $^2J_{H,F} = 42$ Hz, $^3J_{H,F} = 4.8$ Hz) ppm. δ_H 5.7 (d of q) ppm.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft for financial support of this work.

References

1 A. Dimitrov, H. Stewig, St. Rüdiger and L. Kolditz, *J. Fluorine Chem., 47* (1990) 13.
2 A. Dimitrov, St. Rüdiger and M. Bartoszek, *J. Fluorine Chem., 47* (1990) 23.
3 A. Dimitrov, W. Radeck, St. Rüdiger and V. Platonov, *J. Fluorine Chem., 52* (1991) 317.
4 A. Dimitrov, St. Rüdiger and J. Pauli, *J. Fluorine Chem., 66* (1994) 223.
5 *Houben-Weyl, Methoden der Organische Chemie,* 4 Auflage, Band V/3 (Halogenverbindungen), Georg Thieme Verlag, Stuttgart, 1962, p. 641.
6 A. Dimitrov, W. Radeck, St. Rüdiger and O. Bechstein, *J. Fluorine Chem., 60* (1993) 57.
7 A. Dimitrov, St. Rüdiger, N. Ignatyev and S. Datcenko, *J. Fluorine Chem., 50* (1990) 197.