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Mechanistic studies on the electrochemical fluorination of trialkylamines and tetraalkylammonium salts [1]

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Abstract

The comparative electrochemical fluorination (ECF) of selected trialkylamines and tetraalkylammonium salts was studied in order to obtain experimental data allowing a precise valuation of the ECF mechanism. The results of the investigation favour the ECF mechanism already proposed by Simons, via oxidation of $F^-.(HF)_n$ to F^- and nHF, as probably the only relevant electrochemical process at the anode. For the first time some experimental proof has been obtained that a direct electrochemical oxidation of the substrate can be ruled out as a decisive step in ECF. © 1997 Elsevier Science S.A.

Keywords: Electrochemical fluorination; Trialkylamines; Tetraalkylammonium salts

1. Introduction

Although the method of electrochemical fluorination (ECF) was discovered more than fifty years ago, by Simons in 1941 [1], and although the process has been widely used since then as a perfluorination method on an industrial scale, its mechanism is disputed in the literature [2–4]. All three known general types of mechanism basically used in electrochemistry have been proposed in attempting to establish the true ECF mechanism. It has been suggested that elemental fluorine is generated electrochemically at the anode and reacts with the organic substrate [1,2]. Anodic formation of high valent nickel fluorides [3] as well as direct electron transfer [4] from the substrate to the anode have been discussed too.

Usually, ECF results in low to moderate yield of the perfluoro compound bearing the starting skeleton structure, and the electric current applied is consumed further by the formation of the well known by-products [5], such as the following: (i) highly fluorinated compounds, bearing mainly one or two hydrogens at the α-carbons with respect to nitrogen if amines or N-containing compounds have been used as starting materials for ECF; (ii) gaseous by-products stemming from cleavage reactions (NF_3, CF_4, CHF_3, etc.); (iii) partially fluorinated compounds remaining dissolved in the HF; (iv) by-products stemming from cleavage, dealkylation, alkylation, isomerization, dimerization, coupling and cyclization reactions, which can be found among the crude product (CP) and HF soluble compounds, as well. Because the substrate undergoes several simultaneous sequences ((i)–(iv)), not necessarily all the steps being electrochemical in nature, but certainly all of them occurring at the anode and leading to a permanent and poorly reproducible change on the surface of the Ni anode, electrochemical studies are not suitable for clarification of the mechanism of the substitution perfluorination reaction.

Indeed, while all published results in the literature obtained from electrochemical studies [6] are in good accordance with a mechanism where the adsorption and charge transfer of the fluoride anion take place, there is no experimental evidence supporting a direct charge transfer from the adsorbed organic molecule to the anode. The known small deviation in the 'current–potential' behaviour of the Ni anode in the presence or absence of an organic substrate is certainly caused by the continuous liberation of gas bubbles at the anode in the former case owing to the anodic cleavage reaction.

2. Results and discussion

If the electrochemistry is limited to showing the discharge of the adsorbed fluoride anions [6], obviously the detection

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[1] Dedicated to Professor Peter Sartori on his 65th birthday.

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and characterization of intermediate species will be a valuable key to understanding and clarifying the ECF mechanism. Thus, we carried out the comparable ECF of selected trialkylamines and tetraalkylammonium salts, searching for such intermediate species which would enable us to give unambiguous answers concerning their formation. The amines submitted to ECF (Table 1) were chosen for these purposes considering some characteristic parts of their molecules.

For example, ECF of the Ishikawa reagent (**5**) was performed because of the existence of a β-hydrogen in the otherwise perfluorinated propyl chain. Looking in particular for its fate during ECF, we can answer the question whether the acidity of the hydrogen to be substituted by fluorine is of importance for the ECF mechanism. If the two-electron transfer EC_bEC_n mechanism holds, this hydrogen, which is doubtless the most acidic in the molecule, should be substituted very easily, very selectively and very quickly [12].

Fig. 1 shows the GC compositions of the CP and of the HF phase from ECF of **5**. From the HF soluble compounds exclusively, compounds containing this hydrogen have been identified by GC/MS, although several hydrogen atoms are already substituted by fluorine in the two ethyl groups (Fig. 1(a) and Table 2). That means that the most acidic hydrogen easily survives the ECF process and can be found in some of the compounds bearing one or two hydrogen atoms in the CP mixture (Fig. 1(b)). The distinction between the different H-containing isomers in CP can be made easily by MS, as demonstrated in Fig. 2 for two examples. The specific MS fragmentation patterns reveal clearly the positions of the hydrogen atoms: $m/e = 284$ vs. $m/e = 302$ are the fragments due to the characteristic β-cleavage fragmentation of the propyl chain, $(M–C_2F_5)^+$ or $(M–CF_3CHF)^+$ respectively. Other important fragments are these containing the nitrogen with all three α-carbons: $m/e = 164$ represents the perfluoro

Table 1
ECF results

Starting compound	CP compounds	Yield [a] (mol%)
$N(CH_3)_3$ [b] **1**	$N(CF_3)_3$ **8**	3.0 [c]
	$(CF_3)_2NCF_2H$ **9**	0.6
	$CF_3N(CHF_2)_2$ **10**	0.2
	$N(CHF_2)_3$ **11**	0.04
	$(CF_3)_2NCF_2CF_3$ **12**	0.04
	$(CF_3)(C_2F_5)NCF_2H$ **13**	<0.01
$C_2H_5N(CH_3)_2$ [d] **2**	$(CF_3)_2NCF_2CF_3$ **12**	11.0
	$(CF_3)(C_2F_5)NCF_2H$ **13**	0.4
	$C_2F_5N(CHF_2)_2$ **14**	0.1
	$N(CF_3)_3$ **8**	1.7
	$(CF_3)_2NCF_2H$ **9**	0.1
$N(CH_3)_4Cl$ **3**	$N(CF_3)_3$ **8**	4.0
	$(CF_3)_2NCF_2CF_3$ **12**	4.0
	$(CF_3)_2NCF_2H$ **9**	0.8
	$CF_3N(CHF_2)_2$ **10**	0.3
	$(CF_3)(C_2F_5)NCF_2H$ **13**	0.04
$N(C_2H_5)_3$ [e] **4**	$N(C_2F_5)_3$ **15**	35.0
	$CF_3CFHN(C_2F_5)_2$ **16**	2.8
$CF_3CFHCF_2N(C_2H_5)_2$ **5**	$N(C_2F_5)_3$ **15**	1.3
	$C_3F_7N(C_2F_5)_2$ **17**	19.1
	$CF_3CFHN(C_2F_5)(C_3F_7)$ **18**	0.7
	$CF_3CFHCF_2N(C_2F_5)_2$ **19**	0.7
	$(CF_3CFH)_2NC_3F_7$ **20**	0.2
	$(CF_3CFH)(CF_3CFHCF_2)NC_2F_5$ **21**	0.3
$CClFHCF_2N(C_2H_5)_2$ **6**	$N(C_2F_5)_3$ **15**	7.3
	$CF_2ClCF_2N(C_2F_5)_2$ **22**	16.1
	$CF_2ClCF_2N(C_2F_5)(CF_3)$ **23**	3.6
	$CF_2ClCF_2N(C_2F_5)(CFHCF_3)$ **24**	3.9
	$C_2F_5N(CF_2CF_2Cl)_2$ **25**	1.2
$N(C_2H_5)_4I$ [f] **7**	$N(C_2F_5)_3$ **15**	38.3
	$CF_3CFHN(C_2F_5)_2$ **16**	1.5

[a] Yield calculated from the total CP amount and GC content of the actual compound.
[b] ECF of **1** reported in [7].
[c] In comparison with the low average ECF yields of **8**, yields as large as 20% for **8**, obtained by the elemental fluorination of **1**, have been reported [8].
[d] ECF of **2** reported in [9], yields taken from [9].
[e] ECF of **4** reported in [10].
[f] ECF of **7** reported in [11].

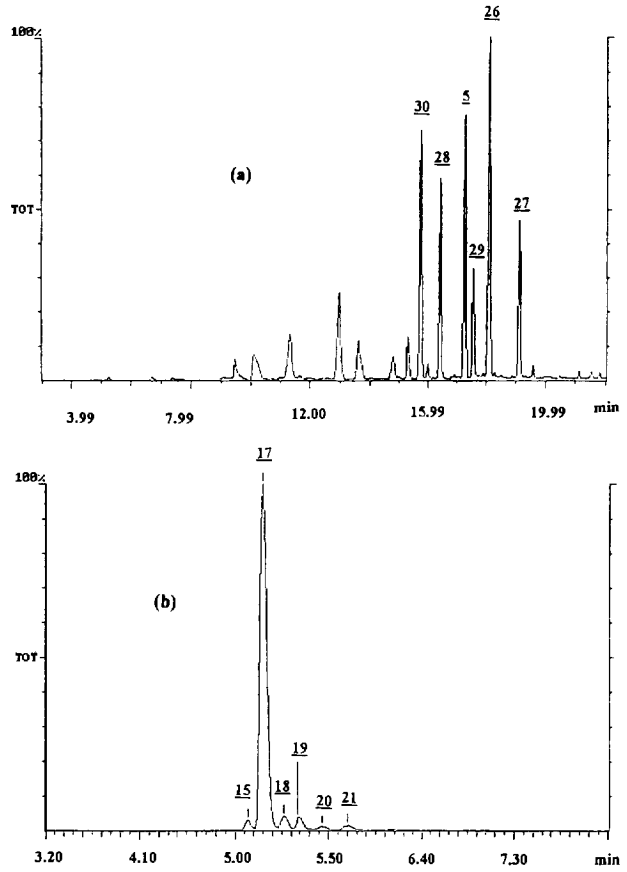


Fig. 1. Gas chromatogram of the HF phase (a) and CP (b) incorporating GC/MS analysis data (samples from ECF of **5** after 100% of the current had been passed).

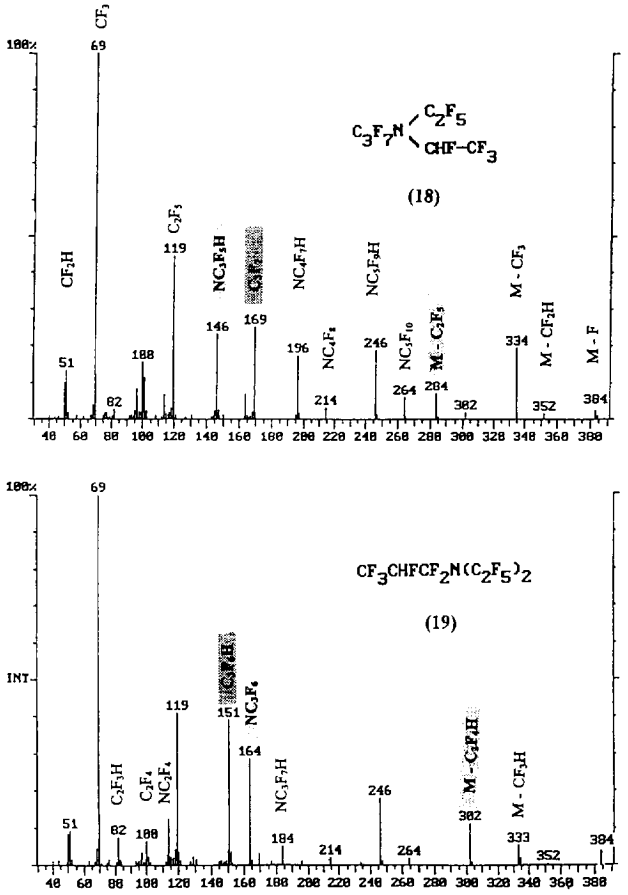


Fig. 2. EI mass spectra of **18** and **19**.

fragment, whilst $m/e = 146$ shows one hydrogen at this position of the molecule. $m/e = 169$ is the perfluorinated propyl radical vs. $m/e = 151$, the starting propyl radical. Additionally the characteristic differences in the ^{1}H and ^{19}F NMR signals caused by the –CHF– fragments [13] in both molecules undoubtedly show the individual isomers (see Section 3). The HF soluble compounds stemming from a progressive replacement of hydrogen by fluorine in **5** but with the β propyl hydrogen not yet substituted have been identified by GC/MS (Table 2) only. In contrast to the other compounds in Fig. 1(a), their mass spectra do not contain the mass fragment $C_2F_5^+$ but show an intensive $C_2F_4H^+$ mass peak. Their common mass fragmentation patterns (Table 2) indicate the fluorine distribution in the two ethyl groups by the progressive fluorination of **5**.

On the strength of GC/MS data (Fig. 1(a) and Table 2), the preferential introduction of the first four fluorine atoms at the β carbon atoms in the two ethyl groups found during ECF of **5** is in agreement with a free radical fluorination process. In a successive ECF substitution reaction a fluorine atom should attack hydrogen in **5**, followed by further fluorination. If carbon or nitrogen are targets for the fluorine radicals, cleavage, dealkylation, alkylation, isomerization, dimerization, coupling and cyclization reactions should follow [8]. A hydrogen attack by F at the β-carbons of the two ethyl groups of **5** is highly favoured, not only statistically but also because the electron withdrawing effects of the quaternary nitrogen in the protonated **5** as well as of the fluorine atoms in the CF_3CHFCF_2– part of **5** should prevent the α- and the propyl β-hydrogen atoms from leaving with their electrons to form HF [10]. However, our results are in disagreement with an ECF mechanism which involves an electrochemical oxidation of the carbon atom carrying the most polarized C–H bond (bearing the highest electron density, possessing the most acidic hydrogen atom) [12]. **5** fulfils all criteria required for favourable electrochemical oxidation of its β propyl carbon atom. The most stable first carbon centred radical should also with certainty be expected to be the precursor radical, leading in a following fluorination step to the perfluoro propyl group in **5**. Its formation is favoured (EC_bEC_n) or not favoured (free radical fluorination mechanism). Our results indicate that only the latter mechanism comes into question in figuring out the true mechanism of ECF.

The most important result from ECF of the Yarovenko reagent (**6**) was the fact that in comparison with the other starting compounds the ECF of **6** produces the highest amount of the expected 1H by-product **24** (Table 1). Consequently, the large chlorine atom in **6** is suppressing, somehow, the substitution of the last hydrogen by fluorine. The question arose whether this chlorine atom would be able to stabilize

Table 2
EI mass spectra of selected compounds from Fig. 1(a) [a]

Compound		5(11H)	26(10H)	27(9Ha)	28(9Hb)	29(8H)	30(7H)
$CF_3CFHCF_2N <$	CH_2–	CH_3	CH_3	CH_2F	CH_3	CH_2F	CHF_2
	CH_2–	CH_3	CH_2F	CH_2F	CHF_2	CHF_2	CHF_2
Relative amount in GC (%)		15.0	19.7	7.8	10.3	5.5	14.6
Fragment							
M–HF		5.0	5.2	–	2.9	–	–
$M–H_2F$	(A)	63.4	68.0	8.6	34.9	4.8	4.7
	A–H	14.9	8.0	–	7.9	–	–
	A–HF	–	6.3	2.3	4.3	5.1	3.9
	$A–H_2F$	–	18.2	11.4	18.8	22.6	3.2
	$A–CH_4$	30.1	4.6	–	3.5	–	–
	$A–CH_3F$	–	41.8	15.6	–	14.5	–
	$A–CH_2F_2$	–	–	–	53.2	25.8	35.4
	$A–C_2H_2F_4$	22.1	10.0	5.9	8.6	13.2	7.0
$M–C_3HF_6$		11.4	9.2	2.2	19.7	3.4	1.2
$M–C_4H_3F_6$		100	64.0	–	56.1	–	–
$M–C_4H_2F_7$		–	100	100	–	100	1.5
$M–C_4HF_8$		–	–	–	100	95.8	100
CF_3CFH		17.5	23.8	15.9	30.8	46.2	29.1
CF_2HCH_2		–	–	–	7.2	9.0	10.0
CF_3		5.3	5.6	4.9	10.6	13.0	5.3
CF_2H		8.6	9.8	7.6	40.3	49.5	31.3

[a] Relative abundance of selected ions in percentage terms. Mass spectra from $m/e = 50$.

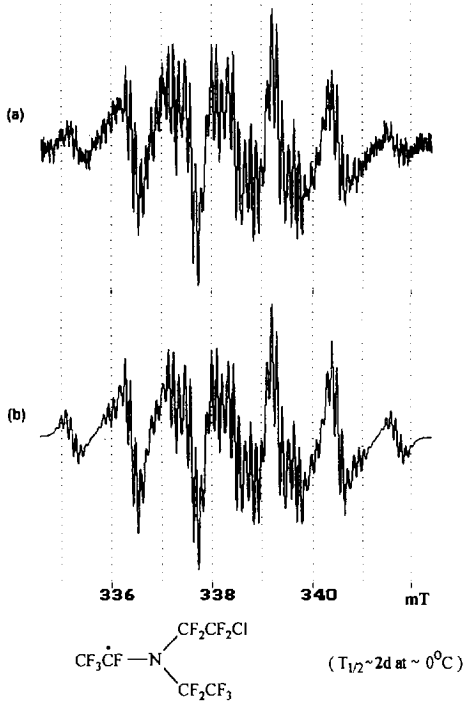


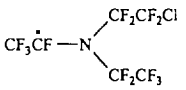
Fig. 3. Experimental (a) and simulated (b) ESR spectra of the radical detected in CP from ECF of **6**.

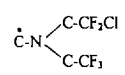
the radical, which is the last in the successive fluorination steps prior to its saturation by fluorine.

Indeed, from the ESR spectrum we were able not only to detect a persistent radical in CP but also to resolve its fine splitting pattern (Fig. 3(a)). The structure of the radical was evaluated by calculations of simulated ESR spectra using the specially written computer program ISOTROP (Bundesanstalt für Materialprüfung und -forschung). The best fit to the experimental spectrum was obtained by computing a 600 line spectrum for the expected radical species formed after the hydrogen abstraction of **24** (Fig. 3(b) and Table 3).

As previously reported [10] during ECF of triethylamine, depending on the current passed, different partially fluorinated triethylamines could be isolated, with the tris(2,2,2-trifluoroethyl)amine (TTEA) being the compound richest in fluorine in the HF layer. It was found further that TTEA, in which all the β-carbon atoms are completely fluorinated, was produced in very low concentrations only. Obviously, the change in physicochemical properties in going from $N(CH_2CF_3)_3$ to $N(CF_2CF_3)_3$ is initiating a drastic increase

Table 3
Values of HF coupling constants used for the simulation of the ESR spectrum as shown in Fig. 3(b)



Nucleus	I	Assignment	HF coupling constant (mT)
$1\times N^{14}$	2/2	–Ċ–N	0.8602
$1\times F^{19}$	1/2	–ĊF–	1.1813
$3\times F^{19}$	1/2	CF_3–Ċ–	1.2062
$4\times F^{19}$	1/2		0.1068
$5\times F^{19}$	1/2		0.0865

in the rate constants of the substitution reactions, leading to the fast consumption of TTEA. One can explain this experimental fact straightforwardly by taking into consideration simply the rate constants of the protonation–deprotonation equilibrium reactions of the partially fluorinated triethylamines. Whereas the low-fluorinated amines are basic enough to allow salt formation, with an increase in the degree of fluorination, the deprotonation reactions become more important, leading to the solvated free amines. The fluorine radicals react at the anode exclusively with the protonated form of the amines until all β-carbon atoms have been perfluorinated, and progressively with the solvated free amines by the further fluorination of the α-carbon. The former reactions proceed with rate constants, as can be estimated with certainty, some orders of magnitude lower than the rate constants of the latter.

In comparing some structural parameters of $N(CH_2CF_3)_3$ with those of $N(CH_2CH_3)_3$ and $N(CF_2CF_3)_3$, one can see that the N–C and the C–C distances are lengthened only in the perfluoro compound [14]. That means that the structural changes on coming from the non-fluorinated amine to the partially fluorinated amine are too small (the only noteworthy change is the increase in the C–N–C angle by 2.5° in the solid or 4.0° in the gas state) and cannot be responsible for a drastic increase in the rate constants of the substitution reactions at the α-carbons. However, the chemical behaviour of TTEA supports very much the experimental results. It is a poor base and a very weak nucleophile [2]. It is protonated in anhydrous HF as proved by ^1H and ^{19}F NMR (after dissolving in HF, δ_H and δ_F of the free amine shift downfield by 2.5 and 4.5 ppm respectively) but it is possible to recover the unprotonated amine simply by pumping off HF even at -10 °C. This shows that the protonation–deprotonation equilibrium reactions indeed become very important for the 'unsteady' kinetics of the substitution reaction at this particular fluorination stage.

We have previously shown that perfluoro-triethylamine can be obtained with comparable ease and in similar yields by ECF either of triethylamine or of tetraethylammonium salts [11]. If, however, the tetraethylammonium cation is submitted to ECF, the rate constants of the substitution reactions cannot be adjusted further by the base strengths of the free amines. In other words, if the ECF of the tetraethylammonium cation is similar to ECF of triethylamine, the splitting off of an ethyl group (non-fluorinated or partially fluorinated) instead of a proton cannot occur by simple interaction with HF. Thus one can expect that the fast consumption of the tris(2,2,2-trifluoroethyl)ammonium moiety should be better inhibited by an alkyl group than by a proton. The results obtained are in good agreement with this. Salts isolated from HF electrolyte (ECF of tetraethylammonium iodide [11] after current has been passed sufficient for the substitution of 15 of the 20 hydrogen atoms present by fluorine) produced, after decomposition with tributyl amine, a very complex mixture of partially fluorinated triethyl amines, with TTEA being one of the main constituents.

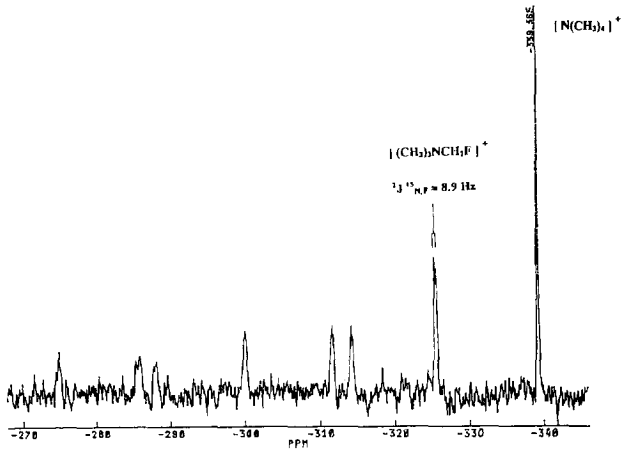


Fig. 4. ^{15}N NMR spectrum of the HF phase from ECF of **3** (sample after 75% of the current had been passed).

The data discussed above give already strong evidence for the radical nature of ECF. However, our results obtained with tetramethylammonium (TMA) salts as starting materials give for the first time some proof that a direct electrochemical oxidation of the substrate can be ruled out as a decisive step in ECF.

Fig. 4 shows the ^{15}N NMR spectrum of the HF phase from ECF of tetramethylammonium cation, recorded directly in HF after current has been passed sufficient for the substitution by fluorine of 9 of the 12 hydrogen atoms present. The results obtained show clearly that the direct anodical oxidation of the tetramethylammonium cation cannot be a decisive electrochemical reaction in ECF. It is well known that the electrochemical oxidation of the tetramethylammonium cation should occur from a carbon–nitrogen bonding orbital (HOMO) leading to cleavage of the carbon–nitrogen bond and consequently to the dealkylation of the tetramethylammonium cation. The protonated trimethylammonium cation resulting from such an oxidation has a ^{15}N chemical shift, which is placed about 15 ppm upfield of the tetramethylammonium signal. However, there were no signals observable upfield from tetramethylammonium. Though there is no evidence for a primary degradation of $[N(CH_3)_4]^+$ to $[HN(CH_3)_3]^+$, the formation of NF_3 throughout ECF as well as the identified $NH_4^+ F(HF)_3^-$ crystals, grown in an HF phase, with a composition identical with the HF phase shown in Figs. 4–6, reveal that the total cleavage of the tetramethylammonium structure takes place continuously. It is unlikely that this cleavage occurs by an electrochemical oxidation of the N–C bond, but if so, it is insignificant for the ECF perfluorination reaction, in comparison with the fluorination of the intact tetramethylammonium structure. From the major compounds of the HF phase, apart from the starting $[N(CH_3)_4]^+$, only $[FCH_2N(CH_3)_2]^+$ has been clearly identified. Its formation can easily be explained in terms of a two-step free radical fluorination; attempts to explain its formation in a four-step anodic process are in principal beyond any reality. The rather resolved ^1H and ^{19}F NMR spectra of the HF phase compounds give strong evidence that most of

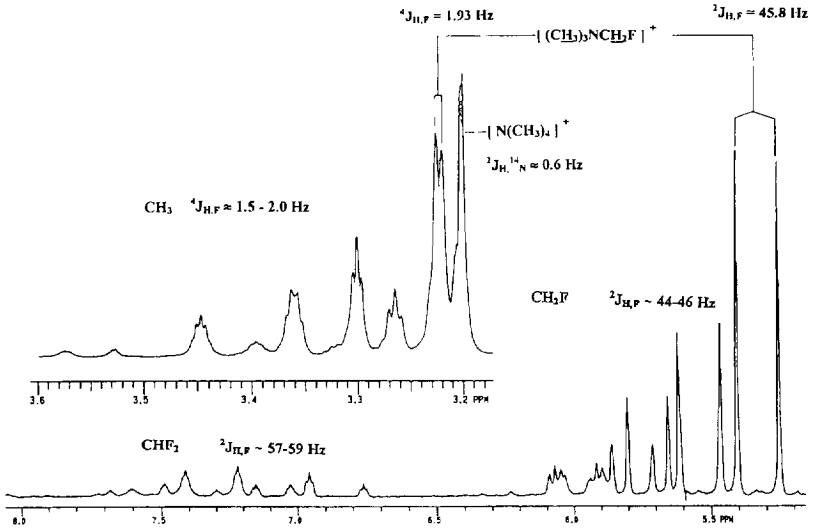


Fig. 5. ^{1}H NMR spectrum of the HF phase from ECF of **3** (sample after 75% of the current had been passed).

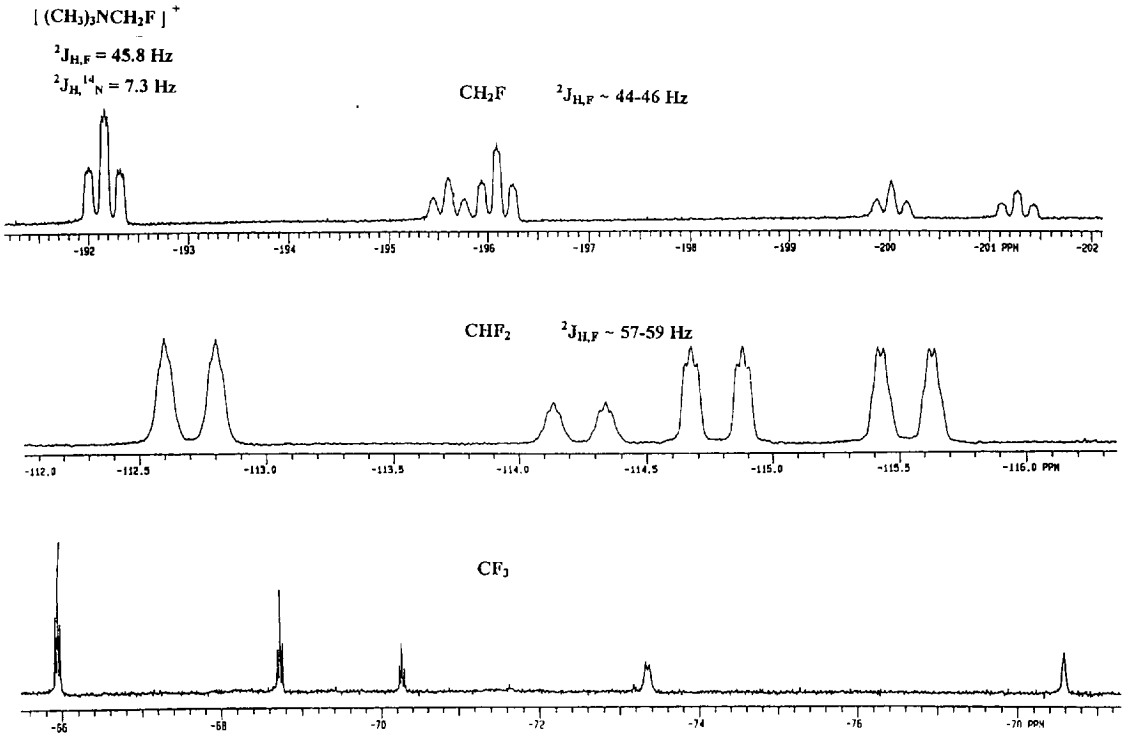


Fig. 6. ^{19}F NMR spectrum of the HF phase from ECF of **3** (sample after 75% of the current had been passed).

the HF soluble species belong to partially fluorinated tetramethylammonium compounds. Most of the chemical shifts and coupling constants [15] are in accord with compounds having fluorinated but intact tetramethylammonium structures (Fig. 5 and Fig. 6). Only the three small signals in Fig. 6 at −66, −68.7 and −70.3 ppm, with triplets of 8.6, 8.7 and 8.8 Hz respectively, are typical of CF_3 groups of 2,2,2-trifluorethyl ammonium compounds. After decomposition of the isolated salts from HF electrolyte by $FCH_2N(CH_3)_2$, we detected by GC/MS exclusively partially fluorinated trimethylamines. Their mass spectra (Table 4) show an identical fragmentation behaviour as **11** [15] and the compounds elucidated by MS are in accordance with those expected from the NMR data. The 2,2,2-trifluorethyl-dimethylamine was the only compound identified among the main constituents of the mixture, which has been liberated from precursor salt or salts formed by an alkyl growth during ECF of **6**. The spectroscopic results make acceptable that $[CF_3CH_2N(CH_3)_3]^+$ and $[CF_3CH_2NH(CH_3)_2]^+$ could both be the precursor cations for its liberation. The two cations might be responsible for the CF_3 signals at −66 and −68.7 ppm respectively (Fig. 6). The former cation might be formed in the very first stage of the fluorination process by a simultaneous attack of $F^\cdot$ and $CF_3^\cdot$ radicals. The latter cation might be the successor of the further fluorination of $[CF_3N(CH_3)_3]^+$, the possible presence of which in the HF electrolyte is supported by the

Table 4
EI mass spectra of partially fluorinated trimethyl-derived compounds [a]

Number of F atoms		3	4	4	4	5	5
Compound		**31**	**32**	**33**	**34**	**35**	**36**
$N(R_1)(R_2)(R_3)$							
R_1		CF_3	CF_3	CHF_2	CHF_2	CF_3	CHF_2
R_2		CH_3	CH_2F	CHF_2	CH_2F	CHF_2	CHF_2
R_3		CH_3	CH_3	CH_3	CH_2F	CH_3	CH_2F
Relative amount in GC (%) [b]		5.2	0.6	47.2	20.3	6.6	3.7
Fragment							
M		43.6	7.9	29.1	11.1	10.8	1.2
M–H		89.8	18.3	23.1	32.5	11.8	11.8
M–F	(A)	81.1	51.0	31.0	25.1	35.2	9.8
	A–CH_4	71.3	8.7	3.6	–	5.2	–
	A–CH_3F	100	100	15.3	24.7	20.8	3.9
	A–CH_2F_2		59.7	56.0	100	71.0	64.5
	A–CHF_3					25.1	47.4
M–CHF_2		–	22.9	93.0	38.2	92.3	21.0
M–CF_3			1.1	91.5	21.8	100	49.1
CF_3		47.0	53.4	3.2	1.3	78.6	4.8
CHF_2		2.1	5.9	100	50.4	90.6	100
CF_2		10.8	12.2	6.8	3.3	18.3	5.8

[a] Relative abundance of selected ions in percentage terms. Mass spectra from $m/e = 50$.
[b] 11.4% $CF_3CH_2N(CH_3)_2$ (**37**) has additionally been found in the mixture.

CF_3 signal at −78.7 ppm [15] (Fig. 6) as well as by the detected $(CH_3)_2NCF_3$ (Table 4). Considering the experimental fact that ECF of $[N(CH_3)_4]^+$ results in a crude product containing $N(CF_3)_3$ and $F_3CCF_2N(CF_3)_2$ in a 1:1 ratio (Table 1), one can suppose that some of the other partially fluorinated trimethylamines detected (Table 4) should also have been liberated from fluorinated tetramethylammonium structures. Our experimental results do not yet allow us to clarify in which quantity and/or distribution of the fluorine the tetramethylammonium structure changes into a tertiary amine or to decide whether the same (randomly) or different (in accordance with structural and electronically principles) precursors are leading eventually to $N(CF_3)_3$ or $F_3CCF_2N(CF_3)_2$.

3. Experimental

ECF experiments, isolation and working up procedures for CP and HF phase compounds were carried out as described elsewhere [5,10,16]. ECF of **1**, **2**, **4**, **7**, together with characterization of **8–16** [7,9–11], as well as the analytical data for the chlorine containing compounds **22**, **23**, **25** [17] have been reported previously.

Gas chromatography was carried out on a Varian 3400 capillary GC machine (60 m column coated with DB5 silicon phase). The same column was used in the GC/MS analysis with a Varian Saturn II system (EI 70 eV).

NMR spectra were recorded at 400 MHz for ^1H, 376 MHz for ^{19}F, and 40.562 MHz for ^{15}N with a Bruker MSL 400 or Jeol JNM-LA400 spectrometer with TMS, $CFCl_3$ and $H^{15}NO_3$ respectively as external standards.

For the ESR measurements an X-band ZWG ERS 300 spectrometer was used.

ECF of **3**. 152.5 g of **3** was electrofluorinated for 90 h in a 1000 ml cell at 5–6 V and 2.5 A dm^{-2}. After 900 A h, ca. 32 g CP (experiment 1 39 g, 2 27.5 g, 3 29 g) were condensed at −78 °C with a GC composition of 47.4% **12**, 38.6% **8**, 7.1% **9**, 2.7% **10** and 0.4% **13**.

In a separate experiment the electrolysis was stopped at 675 A h (at this point 18.5 g CP were condensed from the gas stream) and the HF partially distilled off: from 980 g, after distillation at 35 °C, 232 g electrolyte was obtained and used for the NMR samples and further investigations. The quantitative organic content of the electrolyte was not determined.

Single crystals were grown at −78 °C and X-ray determined, but only the known compound $NH_4^+ F(HF)_3^-$ was found [18].

Samples of 10–20 ml of this electrolyte were treated with 20–50 ml BF_3-diethylether adduct, the precipitate was filtered off, washed with ether and dried in vacuum. The salts were treated with $FCH_2N(CH_3)_2$ (synthesized in accordance with Ref. [19]) or with 5% solution of $FCH_2N(CH_3)_2$ in dioxane and GC/MS investigated (Table 4).

The same procedure as above was used in working up the HF phase from ECF of **7**. However, the decomposition of the tetrafluoroborate salts was performed with tributyl amine.

ECF of **5**. 50 g of **5** (Fluorochem ABCR) was electrofluorinated at 5–6 V and 2 A dm^{-2} in a 450 ml cell. After 135 A h, 21 g CP was obtained with a GC composition of 85.7% **17**, 5.2% **15**, 3.2% **18**, 3.1% **19**, 1% **20** and 1.5% **21**. After separation of CP, the HF was distilled off from the electrolyte at 50 °C, the remainder of ca. 10 g was treated with 2%

solution of K_2CO_3, the organic layer separated, dried with Na_2SO_4 and GC/MS investigated (Table 2).

ECF of **6**. 50 g of **6** (Fluorochem ABCR) was electrofluorinated at 5–6 V and 1.5 A dm^{-2} in a 450 ml cell. After 140 A h, 24.1 g CP was drained off from the cell and 8 g condensed at −78 °C. The combined 32.1 g CP had a GC composition of 51.4% **22**, 22.4% **15**, 10% **23**, 11.8% **24** and 4% **25**.

3.1. Analytical data

17. $CF^a_3CF^b_2CF^c_2N(CF^d_2CF^e_3)_2$. ^{19}F NMR: δ_F ^{a}(3F) −82.3 ppm, ^{b}(2F) −122.3 ppm, ^{c}(2F) −85.4 ppm, ^{d}(4F) −89.3 ppm, ^{e}(6F) −82.1 ppm. MS data: 402[M–F], 352[M–CF_3], 302[M–C_2F_5], 164[NC_3F_6], 169[C_3F_7], 119[C_2F_5](BP).

18. $CF_3CFHN(C_3F_7)(C_2F_5)$. MS data: see Fig. 2(a). NMR data: δ_H 5.75 (d of q, $^2J_{H,F}$=42 Hz, $^3J_{H,F}$=4.8 Hz) ppm; δ_F −160.8 (d of m) ppm.

19. $CF_3CFHCF^aF^bN(CF_2CF_3)$. MS data: see Fig. 2(b). NMR data: δ_H 5.06 (d of d of d of q, $^2J_{H,F}$=44 Hz, $^3J_{H,Fa}$=19.1 Hz, $^3J_{H,F}$=5.4 Hz, $^3J_{H,Fb}$=1.8 Hz) ppm; δ_F −205.8 (d of m) ppm.

20. $C_3F_7(CFHCF_3)_2$. MS data: 366[M–F], 316[M–CF_3], 266[M–C_2F_5], 128[$NC_3F_4H_2$], 169[C_3F_7], 101[C_2F_4H], 69[CF_3](BP)

21. $CF_3CFHCF_2N(CFHCF_3)(CF_2CF_3)$. MS data: 366[M–F], 316[M–CF_3], 284[M–C_2F_4H], 146[NC_3F_5H], 151[C_3F_6H], 119[C_2F_5], 101[C_2F_4H], 69[CF_3](BP).

24. $CF_3CFHN(C_2F_5)(CF_2CF_2Cl)$. NMR data: δ_H 5.5 (d of q, $^2J_{H,F}$=42 Hz, $^3J_{H,F}$=4.6 Hz) ppm; δ_F −161 (d of m) ppm. MS data: 350[M–F], 300[M–CF_3], 284[M–CF_2Cl], 146[NC_3F_5H], 135[C_2F_4Cl], 119[C_2F_5], 101[C_2F_4H], 85[CF_2Cl], 69[CF_3](BP).

37. $CF_3CH_2N(CH_3)_2$. MS data: 127[M], 126[M–H], 110[CF_3CHNCH_2], 83[CF_3CH_2], 76[M–CHF_2], 69[CF_3], 58[M–CF_3](BP).

References

[1] J.H. Simons, *Fluorine Chemistry*, Academic Press, New York, 1950.
[2] St. Rüdiger, A. Dimitrov and K. Hottmann, *J. Fluorine Chem., 77* (1996) 155.
[3] P. Sartori, N. Ignat'ev and S. Datsenko, *J. Fluorine Chem., 75* (1995) 157.
[4] G.P. Gambaretto, M. Napoli, L. Conte, A. Scipioni and R. Armelli, *J. Fluorine Chem., 27* (1985) 149.
[5] A. Dimitrov, H. Stewig, St. Rüdiger and L. Kolditz, *J. Fluorine Chem., 47* (1990) 13.
[6] A. Dimitrov, St. Rüdiger, N. Ignatyev and S. Datcenko, *J. Fluorine Chem., 50* (1990) 197.
[7] H. Bürger, H. Niepel, G. Pawelke, H.J. Frohn and P. Sartori, *J. Fluorine Chem., 15* (1980) 231.
[8] J.A. Gervasi, M. Brown and L.A. Bigelow, *J. Am. Chem. Soc., 78* (1956) 1679.
[9] H. Bürger, R. Eujen, H. Niepel and G. Pawelke, *J. Fluorine Chem., 17* (1981) 65.
[10] A. Dimitrov, St. Rüdiger, K. Seppelt and T. Peplinski, *J. Fluorine Chem., 68* (1994) 15.
[11] A. Dimitrov, W. Radeck, St. Rüdiger and O. Bechstein, *J. Fluorine Chem., 60* (1993) 57.
[12] H. Meinert, R. Falcker, J. Mader, P. Reuter and W. Röhlke, *J. Fluorine Chem., 51* (1991) 53.
[13] T. Abe, E. Hayashi, H. Baba and Sh. Nagase, *J. Chem. Soc. Jpn.*, (1985) 1980 (in Japanese).
[14] A. Dimitrov, H.-G. Mack, St. Rüdiger, K. Seppelt and H. Oberhammer, *J. Phys. Chem., 98* (1994) 11401.
[15] D.J. Brauer, H. Bürger, M. Grunwald, G. Pawelke and J. Wilke, *Z. Anorg. Allg. Chem., 537* (1986) 63.
[16] A. Dimitrov, W. Radeck, St. Rüdiger and V. Platonov, *J. Fluorine Chem., 52* (1991) 317.
[17] K. Omori, Sh. Nagase, H. Baba, K. Kodaira and T. Abe, *J. Fluorine Chem., 9* (1977) 279.
[18] D. Mootz and W. Poll, *Z. Naturforschung, B, 39* (1984) 290.
[19] H. Böhme and M. Hilp, *Chem. Ber., 103* (1970) 104.