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Electrochemical fluorination (ECF) of trialkylamines – an access to ECF mechanism ☆

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Abstract

Many different types of investigations carried out during or in connection with electrochemical fluorination (ECF) of trialkylamines are discussed in terms of the ECF mechanism. These investigations include the type, properties and kinetics of the formation of perfluorotrialkylamines and of their partially fluorinated intermediates, and also the formation of stable radicals. The results are in favour of an initially kinetically controlled fluorination by the fluorine formed and adsorbed at the Ni/NiF_2 anode.

Keywords: Electrochemical fluorination; Trialkylamines; ECF mechanisms; Photoelectron spectroscopy; Raman spectroscopy; NMR spectroscopy

1. Introduction

Amines were amongst the very first compounds which have been perfluorinated by the Simons process, i.e. by electrolysis in anhydrous hydrogen fluoride on nickel anodes (electrochemical fluorination, ECF) [1]. Subsequently, ECF has proved to be the only useful method for the synthesis of perfluoroamines [2].

In most of the papers and nearly all patent applications dealing with ECF, syntheses of the desired perfluorinated compounds are described [3–5]. Consequently, the only fluorination products reported are those constituting the mixture of crude perfluoro products. The qualitative and quantitative composition of the crude perfluoro products is sometimes discussed in terms of the ECF mechanism [6]. On the other hand, several investigations designed to elucidate the mechanism of ECF were carried out under very special conditions, e.g. a study of the anodic behaviour of nickel in anhydrous HF [7], or even in organic solvents (e.g. acetonitrile), rather than in HF using different fluoride sources and working with platinum anodes [8]. Obviously, conclusions drawn from the latter type of experiments can be of limited value only if the Simons process is being considered. As a consequence, the basic mechanism of the electrochemical anodic process is still controversial. The different mechanisms proposed (see e.g. Ref. [4] and references cited therein) can be divided into three main groups which postulate, respectively: (i) the organic substrate reacts with electrochemically generated fluorine which might be adsorbed at the Ni/NiF_2 surface of the anode; (ii) anodically formed NiF_n with $n > 2$ fluorinates the organic substrate, possibly via a substrate-nickel fluoride-complex; and (iii) direct electron transfer from the substrate to the anode followed by chemical reactions with the solvent (EC_BEC_N) is the key process.

In ECF, yields are mostly moderate or even rather poor. Yet, only limited efforts had been made to detect other types of fluorination product, namely partially fluorinated ones. Instead, regarding ECF as the sole perfluorinating method, a 'zipper mechanism' has been postulated [2,9] to explain the alleged exclusive formation of perfluoro products. According to this postulate, once a molecule is attached to the anode it will be released only if it has become perfluorinated such that one hydrogen is replaced by fluorine, followed by the next hydrogen and the next fluorine, etc., i.e. zipper-like.

For a long time, the only partially fluorinated compounds mentioned in literature reports were those with one or two hydrogen atoms remaining in the molecule occurring as impurities in the mixture of the crude product. Because of their somewhat lower chemical and thermal stabilities, their removal attracted some attention [10]. Later, a study aimed at obtaining the total current balance of ECF revealed that the formation of partially fluorinated compounds as intermediates and also as by-products is an inherent part of ECF, and

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that a substantial amount of current is lost due to partially fluorinated by-products remaining dissolved in the HF [11]. In the cased of trialkylamines, no compounds bearing fluorine at the α-C atoms could be found among all these partially fluorinated by-products [12].

Using ECF for the syntheses of perfluoroamines, we also became aware of the potential that the ECF of amines holds for obtaining a deeper insight into the mechanism of ECF. A comprehensive evaluation of our results in terms of ECF mechanism is given in this paper.

2. Results and discussion

The occurrence of intermediates during ECF provides evidence that the perfluorination reaction proceeds stepwise via partially fluorinated intermediates which are repeatedly adsorbed anodically – and thereby fluorinated – and desorbed [11–13]. The kinetics of an ECF experiment can therefore be described in terms of a sequence of reactions. Initially, only the non-fluorinated, protonated and consequently positively charged molecules of the substrate amine are attached to the anode in a dynamic equilibrium ('attached' is preferred to 'adsorbed' because the latter is unlikely due to the equal charges of the molecules and the anode). Molecules which have become fluorinated at the anode, i.e. one H atom being replaced by F, are also likely to become displaced. Thus, there is competition between the molecules dissolved in the HF at the anode to become fluorinated, depending on their relative concentrations and on their respective physicochemical properties. These kinetics are confirmed by changes in the concentration profile of the H-amine to be fluorinated as well as of the partially fluorinated amines formed when increasing amounts of current are passed through the cell. When the concentrations are plotted versus the current passed, one obtains a picture which is typical for subsequent reactions: whereas the H-amine declines logarithmically [14], the partially fluorinated amines behave differently as shown in Fig. 1 for the ECF of triethylamine (TEA) (the data used are identical with those given in Ref. [15]). From Fig. 1 it follows that amines with one or two F atoms reach a peak concentration quite quickly, followed by a steep decline obviously because of further fluorination. Amines with three F atoms also rapidly reach their (lower) maximum concentration which remains at a (roughly) constant level over a prolonged period. Amines with four F atoms can be detected early but their concentration increases further. Amines with 5–9 F atoms can be found rather late in the electrolysis process in the HF because they are the successors of the lower fluorinated amines, but some of them (4F, 5F, 6F) are present in relatively high concentration.

From the arguments given, it follows that the physicochemical properties of the partially fluorinated intermediates – or more precisely, the course of these properties with progressive fluorination – provide a clue to a better understanding of the ECF process, which is probably as important as the anodic electrode process.

As mentioned above, the HF from the ECF of trialkylamine contains all types of fluorinated amines except those with fluorine at the α-C atoms. In the case of TEA, tris(2,2,2-trifluoroethyl)amine (TTFEA) is the highest fluorinated compound which can be found dissolved in HF [15]. Obviously, an introduction of a further F atom, necessarily at an α-C, causes decisive changes in the molecule. Hence, TTFEA was selected for a comparison of some of its data with those for non-fluorinated (TEA) as well as perfluorinated triethylamine (FTEA).

In its chemical behaviour, TTFEA comes between TEA and FTEA. Like TEA, its basicity is sufficiently high for it to dissolve in anhydrous HF (AHF) under protonation, as indicated by a shift in the ^{1}H NMR spectrum from 3.29 ppm (neat TTFEA) to 4.37 ppm (in AHF), but like FTEA its nucleophilicity is so low that it could not be quarternized.

A measure of the electron density at the nitrogen atom of the three amines under consideration was expected from ^{15}N NMR measurements. The ^{15}N chemical shifts are [16] ($H^{15}NO_3$: $\delta = 0$ ppm): $N(CH_2CH_3)_3$ (TEA) $\delta = -332.5$ ppm; $N(CH_2CF_3)_3$ (TTFEA) $\delta = -376$ ppm; and

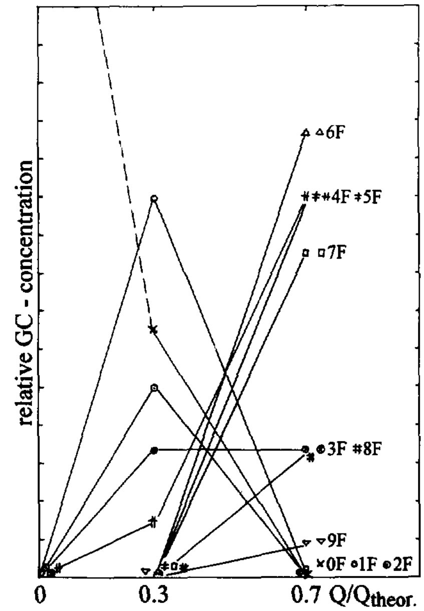

Fig. 1. Dynamics of the ECF of TEA: concentrations of TEA and of $(CH_{3-k}F_kCH_2)(CH_{3-m}F_mCH_2)NCH_2CH_{3-n}F_n$, with $k+m+n = 1$–9, during the course of ECF.

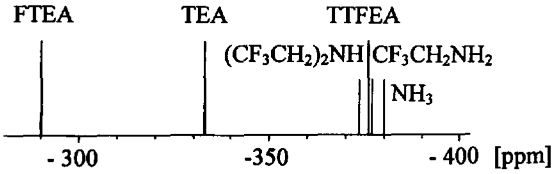

Fig. 2. Schematic representation of the ^{15}N NMR chemical shifts of TEA (triethylamine), TTFEA [tris(2,2,2-trifluoroethyl)amine] and FTEA (perfluorotriethylamine) together with $(CF_3CH_2)_2NH$, $CF_3CH_2NH_2$ and NH_3.

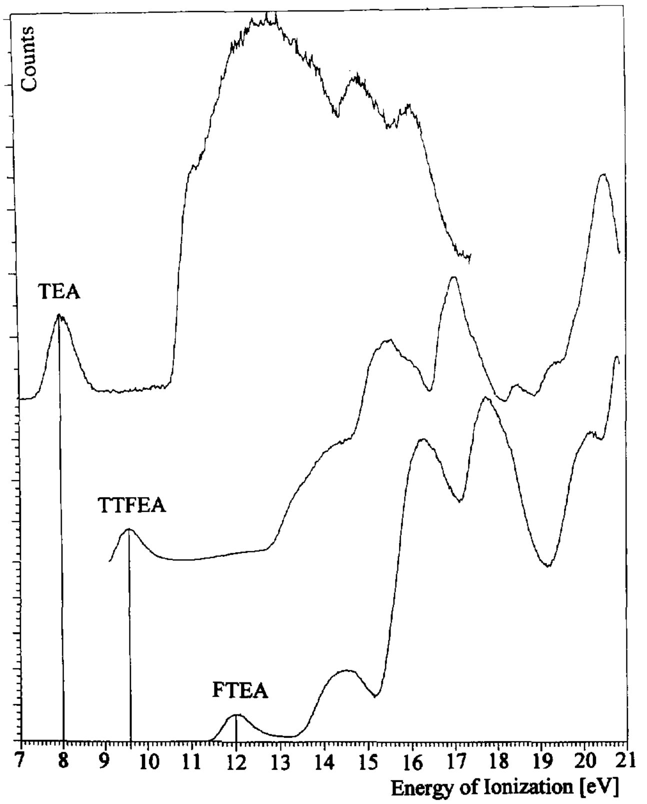

Fig. 3. He^I photoelectron spectra of TEA (triethylamine), TTFEA [tris(2,2,2-trifluoroethyl)amine] and FTEA (perfluorotriethylamine).

$N(CF_2CF_3)_3$ (FTEA) $\delta = -290.1$ ppm. In addition, the shifts for $(CF_3CH_2)_2NH$ and for $CF_3CH_2NH_2$ were determined as -373.7 ppm and -377 ppm, respectively, i.e. close to NH_3 with $\delta = -380$ ppm (Fig. 2). As expected, the N in FTEA resonates at the lowest field since the N nucleus is the lowest shielded. However, the succession between TEA and TTFEA is somewhat surprising, since TTFEA resonates at distinctly higher field than TEA. In fact, the influence of CF_3CH_2 groups on nitrogen shielding is very similar to that of hydrogen, as a comparison between ammonia, 2,2,2-trifluoroethylamine and bis(2,2,2-trifluoroethyl)amine shows. Obviously, the ^{15}N chemical shift data do not reflect the chemical behaviour (concerning basicity and nucleophilicity) of the amines, because the latter is more specifically related to the nitrogen lone pair.

Direct information about the lone pair was obtained from photoelectron spectroscopy (PES) [16]. Fig. 3 shows the He^I photoelectron spectra of TEA, TTFEA and FTEA. The lowest ionization potential, corresponding to the adiabatic ionization of the nitrogen lone pair, shows a reasonable progression. It is lowest for TEA, 8.0 eV, indicating a relatively high electron density for this orbital. In TTFEA, the nine F atoms present reduce (due to their known inductive effect) the availability of the nitrogen lone-pair electrons, and consequently the adiabatic ionization energy is increased to 9.6 eV. The latter effect becomes more dominant with the replacement of the last six H atoms next to the nitrogen by F in FTEA; the ionization energy for FTEA amounts to 12.0 eV. Thus, the PES n_N-ionization potentials are in accordance with the chemical behaviour, with the F atoms at α-C atoms having a much greater influence than those at β-C atoms. Similar to the ^{15}N NMR spectroscopic data, the lone-pair ionization potentials of ammonia (10.15 eV), 2,2,2-trifluoroethylamine (10.35 eV) and bis-(2,2,2-trifluoroethyl)-amine (10.1 eV) are quite close together and to that of TTFEA, but their chemical properties differ markedly. Hence, a relation between the latter and the PES ionization energy must only apply among analogous types of amines.

The increase in PES n_N-ionization potentials in going from TEA through TTFEA to FTEA corresponds well with the increase in the electrochemical oxidation potential, moderated of course by the solvent MeCN, in going from TEA to TTFEA (1.24 V versus Pt/H_2 [17]) and to FTEA, and similarly from dibutylmethylamine (DBMA) to partially fluorinated DBMA and to the perfluorinated form, with the latter being too high to be measurable in MeCN [14]. It is reasonable to assume that there is a similar but probably smaller increase in the electrochemical oxidation potential of protonated amines with the introduction of increasing numbers of F atoms, but their oxidation potentials are too high for organic solvents. Under ECF conditions, however, i.e. in AHF at Ni electrodes, the working potential does not depend on the type of substrate dissolved [14]. Consequences of this phenomenon will be discussed later in this paper.

The geometric structure of the compound to be fluorinated by ECF is of interest because that part of the molecule which is nearest to the anode is likely to become fluorinated first [18]. However, the geometric structure might change with the degree of fluorination, as a comparison of TEA with TTFEA and FTEA shows.

According to gas electron diffraction (GED) investigations [19], TEA has three conformers with C_3, C_1 and C_s symmetry and their populations are 56%, 33% and 11%, respectively. The ethyl groups of TEA are all synclinal to the nitrogen lone pair in the C_3 conformer, but in the C_1 and C_s structures one ethyl group is in an antiperiplanar position and the other two groups possess synclinal orientations. The main C_3 conformer has CNC angles of 112.6°.

According to GED analysis [20], TTFEA with its fluorinated methyl groups has a predominantly C_1 structure, but small contributions due to C_s and/or C_3 conformers might be present, their respective energies according to ab initio calculations being 0.7 kcal mol^{-1} and 3.6 kcal mol^{-1} higher than that of the C_1 conformer. In the main conformer, the CNC angles are 116.6°, indicating a partial flattening of the NC_3 pyramid, with two of the CF_3CH_2 groups possessing synclinal orientation to the nitrogen lone pair which they nearly eclipse. This shielding of the lone pair and its reduced availability due to the inductive effect of the trifluoromethyl groups may explain the non-reactivity of TTFEA towards nucleophiles. The Raman spectra of liquid TTFEA have shown [20] that two conformers are also present in the liquid state. A more detailed evaluation of the temperature-dependent changes in the Raman spectra, applying the procedure

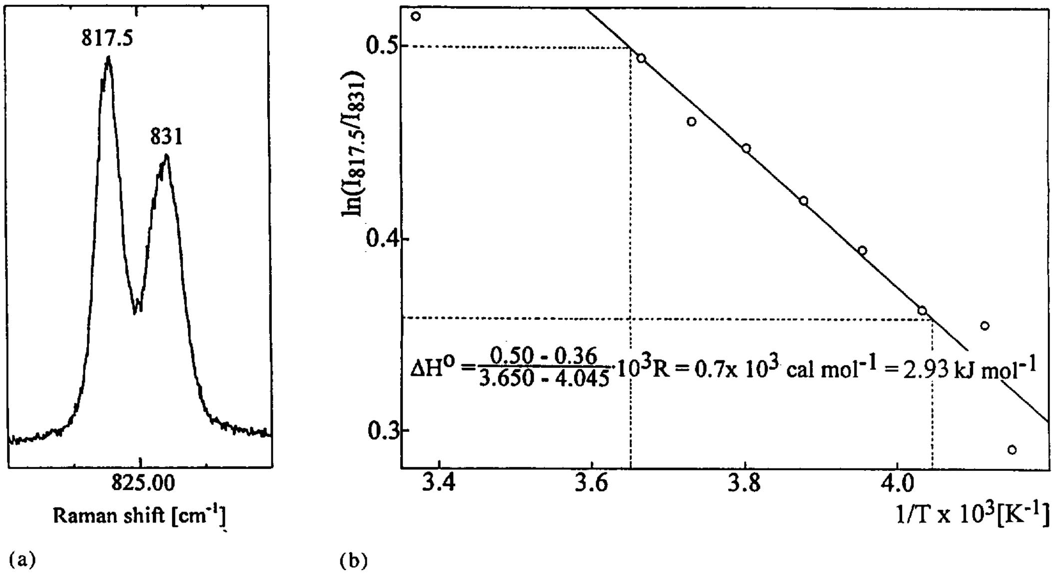

Fig. 4. (a) Detail of the Raman spectra of liquid TTFEA [tris(2,2,2-trifluoromethyl)amine] at −35 °C. (b) Ratio of the respective amplitudes of the 817.5 cm^{-1} and the 831 cm^{-1} signals plotted against the reciprocal of the temperature.

given in Ref. [21], revealed an energy difference between these conformers of 0.7 kcal mol^{-1} (see Fig. 4), indicating that the C_1 and C_s conformer should also be present in the liquid as in the gaseous state.

A more obvious structural change occurs if the CH_2 groups are also fluorinated. GED analysis of FTEA [22] revealed C_3 symmetry, the NC_3 being nearly in a plane with CNC angles of 119.3°, but all three pentafluoroethyl groups are anticlinally oriented with respect to the nitrogen lone pair.

The above comparisons between TEA, TTFEA and FTEA, which are summarized in Table 1, demonstrate the enormous changes in the amine molecules as fluorination proceeds. The very different molecules formed during the process are competitors as well as successors in the fluorination process, whose mechanism cannot be identical for all these molecules. Whereas the process is kinetically controlled as discussed above at an early stage of fluorination, the situation changes later. Tertiary amines fluorinated to such a high degree that fluorine is introduced at the α-C atoms (e.g. fluorinated TEA with 10 or more F atoms) become insoluble in AHF ('HF-phobic') but soluble in perfluorocarbons ('PFC-philic'). They can be found as H-containing by-products in the crude perfluoro products. As a result, these molecules have limited chances – only by the help of partially fluorinated surface-active products [23] – to leave the anode surface. As a result of a kind of 'HF-phobic interaction' with the anode rather than specific adsorption, they should remain at the anode and become predominantly fluorinated, i.e. a kind of 'zipper' mechanism might be effective at this fluorination stage. Specific adsorption can be excluded because otherwise the anode would become blocked by perfluorinated products within a short time. Droplet formation by 'PFC-philic interaction' together with the emulsifying properties of partially fluorinated products [23] may be decisive for the removal of perfluorinated products from the anode.

As for the basic electrochemical anode process, the first of the three types mentioned above implies that, to a certain extent, ECF should be similar to direct fluorination. In fact, ECF proceeds only at potentials which are high enough for the oxidation of fluoride ions [14,24]. With freshly cleaned neat Ni sheet, an electric current at potentials below 2.9 V also occurs resulting from the formation of a nickel difluoride layer [14,24,25]. On completion of that layer, the current drops nearly to zero although NiF_2 is also conductive at such potentials, probably by a hopping mechanism [26]. The minimum potential necessary for ECF is not influenced by varying amounts of trialkylamine and/or sodium fluoride [14]. In contrast to 'normal' electrochemistry in organic solvents, not only (protonated!) trialkylamines but also tetraalkylammonium compounds can be fluorinated [27]. The latter fluorinate early in the course of the process, i.e. after introduction of only one or a few F atoms [28], splitting off of one alkyl group to yield perfluorotrialkylamine but no perfluorotetraalkylammonium salts.

We found that there is an astonishing similarity between ECF and direct fluorination in that with both methods stable radicals can be obtained. Thus, with diethyl-heptadecafluoro(3-ethyl-2,4-dimethyl-1-pentene)amine, both methods of fluorination gave stable radicals with similar ESR spectra [29], an observation which supports the suggested similarity in the fluorination mechanisms.

An ECF mechanism consisting of the anodic discharge of fluoride ions as the basic step gains further support from the 'open circuit potential'. It is well known that if the ECF cell is disconnected from its current supply during an ECF experiment, the anode potential decays logarithmically over a prolonged period of time [30]. This potential not only causes a substantial back-current if discharged through an external conductor, as we have repeatedly observed [31], but it might also be the reason for prolonged electrofluorination after the

Table 1
Comparison of selected properties of TEA (triethylamine), TTFEA [tris(2,2,2-trifluoroethyl)amine] and FTEA (perfluorotriethylamine)

Property/parameter	TEA	TTFEA	FTEA
Chemical and spectroscopic properties			
Basicity	high	protonated in HF	none
Nucleophilicity	high	none	none
He^I PES: n_N-Ionization [16]	8.0 eV	9.6 eV	12.0 eV
^{15}N NMR [16]	−332.5 ppm	−376 ppm	−290.1 ppm
Geometric parameters (from GED)	[19]	[20]	[22]
Symmetry	$C_3+C_1+C_s$ (56% + 33% + 11%)	C_1 ($+C_s/C_3$)	C_3
Orientation of CH_3 or CF_3 with respect to nitrogen lone pair	C_3: 3*x* synclinal	C_1: 2*x* synclinal	C_3: 3*x* anticlinal
<C–N–C (°)	112.6	116.8	119.3
<N–C–C (°)	112.1	114.7	118.2
N–C (pm)	146.6	143.6	148.2
C–C (pm)	152.8	152.7	159.2

disconnection, i.e. without an external current supply, as recently reported [32].

Consequently, the process at the anode schematically represented in Fig. 5 can be described as follows. Neat nickel is electrochemically oxidized at its surface to Ni^{2+} which subsequently forms NiF_2 as a dense layer which is insoluble in AHF and protects the metal from further attack. The NiF_2 layer is electrically conductive enabling further current flow. At a potential above about 2.9 V, fluoride ions are oxidized to fluorine radicals which become adsorbed at the NiF_2 surface [7,25,33]. Substrate molecules attached to or in the vicinity of the anode may react with the fluorine atoms as depolarizors. Such a radical attack of fluorine explains the formation of CF_4 and NF_3 during ECF as well as stable fluoroorganic radicals, should the occasion arise. If no depolarizor (organic substrate or water as a common impurity) is available, the electrochemical reaction ceases or elemental fluorine is formed at an increased potential, causing the well-known explosions in the undivided cell. The assumption that fluorine atoms are adsorbed in the nickel difluoride layer of the anode leads further to a satisfactory explanation of the 'open circuit potential' [30] as well as of the fluorinating activity after the current is switched off [32].

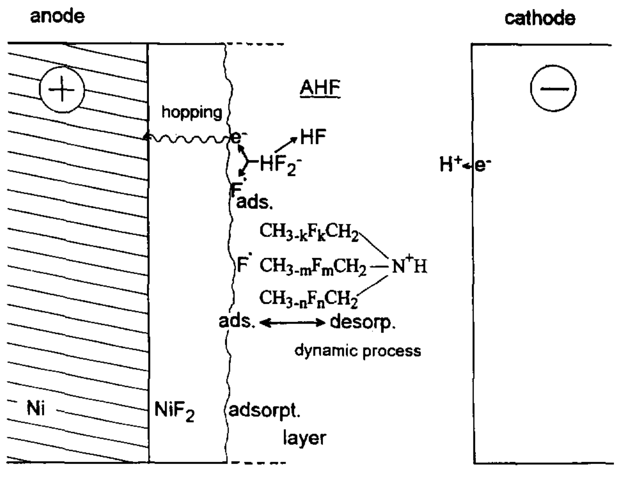

Fig. 5. Schematic representation of the processes occurring at the anode of an ECF cell.

3. Experimental details

The electrochemical fluorination of TEA, as well as the synthesis of TTFEA, have been described previously [15,20]. Attempted quarternization of TTFEA [17] was carried out with CH_3I using a standard procedure with $CH_3I/AgBF_4$ [34], with CH_2N_2/H^+ by a standard procedure and with $C_4F_9SO_2CH_2CF_3$ under conditions described by Dimitrov et al. [20] for the synthesis of TTFEA; they were all unsuccessful.

Temperature-dependent Raman spectra were recorded with a Ramalog (Spex) instrument using an Ar laser (488 and 514 nm) as described elsewhere [20]. Estimation of ΔH^0 for the two conformers present in liquid TTFEA was undertaken as described by Ernst et al. [21]. The two intense Raman bands at 817.5 cm^{-1} and 831 cm^{-1} [Fig. 4(a)] were selected for the determination of the relative populations (taken directly without deconvolution). From thermodynamics, the equilibrium constant (K) may be written as: $\ln K=(\Delta H^0/R)\times 1/T-\Delta S^0/R$. The constant K can be expressed by the ratio of the intensities of the two Raman bands, i.e. $K=I_{817.5}/I_{831}$. Thus, from the slope of the plot of $\ln(I_{817.5}/I_{831})$ versus $1/T$, the value of ΔH^0 can be estimated [Fig. 4(b)].

^{15}N NMR spectra were recorded with a Bruker MSL 400 spectrometer at 40.562 MHz [16]. Photoelectron spectra were obtained using a high-resolution tandem electron spectrometer consisting of two pseudo-spherical electron monochromators, with a helium discharge lamp (21.21 eV). The spectra were calibrated against in argon and xenon ionization, respectively [16].

4. Conclusions

ECF is a rather complex process. Even in case of a comparatively simple substrate such as TEA, many differently fluorinated compounds with very different chemical, electronical and structural properties may be formed during the process. Hence, it is unlikely that a single mechanism applies over all the process. If the differently fluorinated compounds are soluble in HF, they are real competitors in a kinetically controlled reaction. The kinetics must change and become more complicated as compounds fluorinated to a high degree are formed which are insoluble in HF. An important consequence of an at least partially kinetically controlled mechanism is that the relative amounts of those by-products resulting from rearrangement reactions of fluorinated intermediates should decrease if the mean concentration of the intermediates can be reduced. This should be effected by experimental conditions which combine high current densities with low substrate concentrations.

The basic anode process can be best explained by assuming that F adsorbed at the anodic NiF_2 is the fluorinating agent, but direct electrochemical oxidation of the organic molecules in addition cannot be completely excluded.

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