Journal of Fluorine Chemistry, 50 (1990) 197–205

Received. March 21, 1990, accepted. July 17, 1990

INVESTIGATIONS ON THE ELECTROCHEMICAL FLUORINATION OF AMINES

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SUMMARY

Electrochemical investigations of dibutylmethylamine (DBMA) and of polyfluorinated amines derived from DBMA by electrochemical fluorination in anhydrous HF (ECF) were carried out. From the results of these investigations, which gave no evidence of a direct involvement of the organic compounds in the anodic process, and from other experimental facts discussed, it follows that the formation of an 'active fluorine' at the anode is very probably the primary step in the ECF of amines.

INTRODUCTION

In 1949 the electrochemical fluorination in anhydrous hydrogen fluoride (ECF) was developed by Simons [1]. Since then this method has been widely used for laboratory as well as industrial preparations of perfluoro organic compounds [2,3,4,5] The application of this method has obviously not been impaired by the fact that its mechanism remains even today a matter of discussion [3,6]. The different mechanisms proposed can be divided into two main groups. One comprises the EC_BEC_N mechanism (and similar ones) [7,8,9,10] which implies that the first step of the fluorination consists of an electrochemical oxidation of the organic substrate by direct electron withdrawal at the anode. The other group of mechanisms postulates that the primary electrochemical oxidation results in such chemical species which are able to fluorinate the organic substrate (e.g. $F^{\cdot}$, or NiF_x with $x > 2$, or F_2 adsorbed to NiF_2) [3,6,11,12,13]. All the mechanisms have to take into account the special importance of nickel being the anode material. It is, however, not clear whether this is due to a kind of catalysis, as it is well-known for fluorinations with elemental fluorine [14], or because of its chemical stability under the experimental conditions [6], or due to specific properties as e.g. adsorption of organic compounds [15]. Probably, a combination of some of these properties makes nickel unique in ECF. It has generally been accepted that ECF results preferably in perfluorinated compounds. This was explained in the following way: once a molecule of the organic compound is attached to the anode (adsorbed at NiF_2), one H-atom after the other will be replaced by F-atoms ("zipper-like") and after having been completely fluorinated the molecule will be released from the anode [5,6,10]. This supposed perfluorination pathway has been regarded as a support of the EC_BEC_N mechanism [6,10]. However, by our investigations of ECF of dibutylmethylamine [16,17] and aminoethers [18] we showed that the zipper-mechanism does not hold true but partially fluorinated intermediates play an important role. Furthermore, it became obvious that the formation of such partially fluorinated compounds which are almost inert against perfluorination under normal ECF conditions is a normal phenomenon in ECF. These compounds (we called them 'HF-phase') remain at the end of ECF dissolved in the HF, further electrolysis results only in gaseous cleavage products, such as CF_4 and NF_3.

To get further details of ECF mechanism and to find an explanation of the inertness of the 'HF-phase' compounds against electrochemical perfluorination some electrochemical investigations with dibutylmethylamine (DBMA) and its HF-phase have been carried out by us. The results are reported here.

RESULTS AND DISCUSSION

Voltammetric investigations in acetonitrile

According to the EC_BEC_N mechanism the electrochemical properties of the organic compound to be fluorinated by ECF are decisive. Therefore, we measured the oxidation potential of DBMA under different conditions and in comparison with its HF-phase and its crude perfluorination product (FDBMA). The experimental conditions and the results are given in Table 1. DBMA (exp. 1) is oxidized in acetonitrile (AN) solution at a rotating Pt-disk electrode at a potential of 0.94 V (vs. sat. Hg/Hg_2Cl_2-el.). Under the same conditions, the HF-phase of DBMA (i.e. partially fluorinated DBMAs) (exp. 2) is oxidized at 1.81 V. The crude perfluoro DBMA (exp. 3) could not be oxidized in AN, although it contains about 15 % of compounds having one or two H-atoms in the otherwise perfluorinated molecule.

TABLE 1

Voltammetric investigations in acetonitrile (AN)

exp.	electrode	electrolyte	ox.potential vs.Hg/Hg_2Cl_2(sat.)
1	Pt, rotat.	AN/$(Bu)_4NBF_4$+DBMA	0.94 V
2	Pt, rotat.	AN/$(Bu)_4NBF_4$+HF-phase	1.81 V*
3	Pt, rotat.	AN/$(Bu)_4NBF_4$+F-DBMA	2.3 V**
4	Pt, rotat.	AN/$(Bu)_4NBF_4$+DBMA+HBF_4(1:1.5)	2.3 V**
5	Pt, rotat.	AN/$(Bu)_4NBF_4$+HF-phase+HBF_4(1:1.5)	2.3 V**
6	Ni	AN/$(Bu)_4NBF_4$	0.1 V***
7	Ni, pre-electr. in HF	AN/$(Bu)_4NBF_4$	1.5 V***
8	Ni, pre-electr. in HF	AN/$(Bu)_4NBF_4$+DBMA	1.5 V***

* The value will be somewhat lower, if the HF-phase comes from an ECF experiment with still running PFC-production.

** above 2.3 V the electrolyte becomes oxidized.

*** oxidation of Ni.

Since under ECF-conditions the amines are dissolved in HF and therefore protonated, we repeated the measurements of the oxidation potentials in AN solution after addition of HBF_4 (amine: HBF_4 = 1:1.5) (exp. 4 and 5). With the protonated compounds no oxidation could be detected in AN (that is below 2.3 V) neither with DBMA nor with its HF-phase. This result was to be expected since quarternized amines can be oxidized only at very high potentials, furthermore it shows that there are no electrochemically traceable amounts of free amines in equilibrium with the protonated ones. As a consequence, it must be always the protonated amine which undergoes electrochemical fluorination. However, a specific adsorption of protonated and therefore positively charged amines at the anode does not seem to be very likely.

Attempts with nickel as anode material in acetonitrile were not succesful. In acetonitrile, neat nickel is oxidized and dissolved far below the oxidation potential of DBMA (Table 1 exp. 6). If the Ni anode is previously anodically oxidized in anhydrous HF, it will be stable up to 1.5 V (vs.sat.Hg/Hg_2Cl_2-el.) in AN, above 1.5 V it will again be dissolved (exp. 7), independently of the presence of DBMA (exp. 8).

Voltammetric investigations in HF

Freshly prepared clean Ni electrodes are anodically oxidized in anhydrous HF at potentials above + 0.1 V vs. a Ni-cathode (Fig. 1a). However, if the Ni electrodes have been previously used as anodes in HF (with about 300 mA/cm^2 for 10 min), there will be no electric current at potentials below +3.3 V but above this potential the current will rise considerably (Fig. 1b). These results are in agreement with those reported by Watanabe [11]. But, surprisingly, the electrochemical properties of such a Ni electrode remain completely unchanged after addition of DBMA to the HF, indicating that the same electrochemical process takes place at the anode as well in pure HF as in DBMA/HF solution. This observation is astonishing because of the high oxidation potential of the fluoride ion in

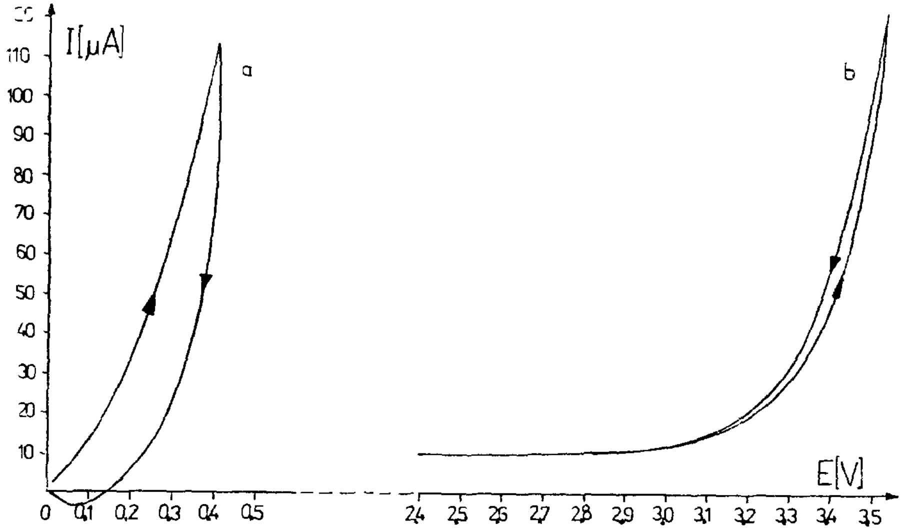

Fig. 1. Cyclovoltammetric investigations with Ni-anodes in HF
a) Freshly prepared and cleaned Ni in HF.
b) Ni previously anodically oxidized in HF. The obtained curves for Ni/HF or for Ni/HF+DBMA are identical.

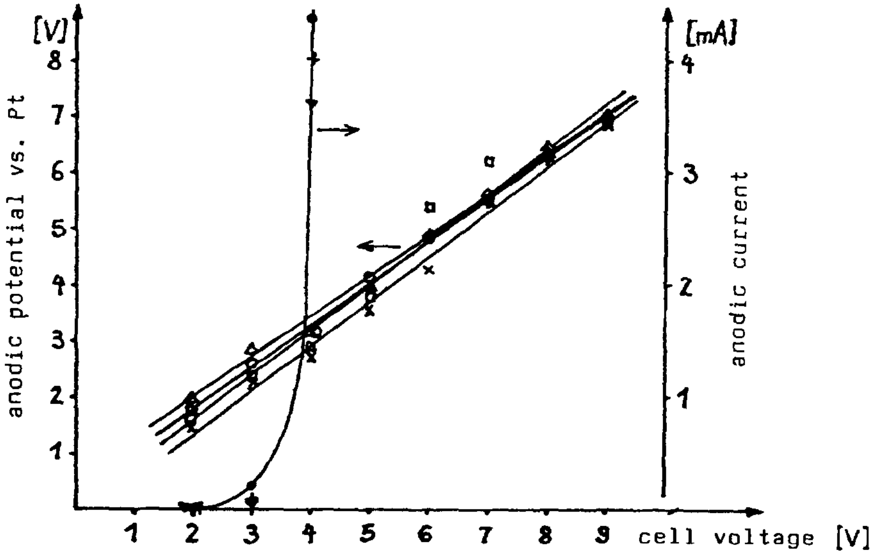

Fig. 2. Anodic potential (<u>vs</u>. Pt) and current as function of cell voltage. Legend: × HF; ○ 0.06 M DBMA/HF; □ 0.34 M DMBA/HF; △0.61 M DBMA/HF; • HF/0.1 M NaF; + HF/0.11 M DBMA + 0.1 M NaF; ▾HF/0.11 M DBMA.

comparison with organic compounds [6]. Possibly, it is due to specific properties of the Ni anode that the oxidation of fluoride ions is favoured against that of the amine.

Independently of these experiments we studied the influence of DBMA on the potential of a Ni anode in HF at increasing cell voltage. Figure 2 shows the dependence of the anodic potential of a Ni electrode (vs. Pt wire as reference electrode) on the applied cell voltage. From Fig. 2 it can be seen that the potential of the Ni anode increases with increasing cell voltage but does not depend on presence and concentration of DBMA.

There is a well-known experimental fact which might also shed some light on ECF mechanism. This is the occurence of small explosions with ECF. These explosions can occur during pre-electrolysis (to remove traces of water from the HF) and during the final period of an ECF experiment. In both cases there are no or virtually no compounds, which can be fluorinated, dissolved in the HF. If one assumes that fluorine (whether atomic or molecular, free or adsorbed) is the real fluorinating agent formed at the anode, then it will become evident that in case of lack of reactants fluorine will be released from the anode and mix with the hydrogen gas. Depending on the concentration of fluorine in hydrogen explosion-like reactions can occur (according to GMELIN [19] F_2/H_2-mixtures with more than about 1 mm Hg F_2 are likely to explode; Wechsberg [20] claims that ECF should be run such a way that the F_2 in the gas stream is kept below 0,1 % to avoid explosions).

Typically, we observed these reactions being not likely to take place in the electrolytic cell or the reflux condenser, which are both made from metal, but in an adjacent polyethylene flask. Probably, the explosion is initiated by light.

Altogether, the results reported here and previously [16, 17] lead to the following conclusions:
(1) The unexpected resistance against perfluorination of the polyfluorinated, HF-soluble compounds remaining at the end of ECF experiments (the HF-phase) is more likely to depend on their structure rather than on their oxidation potential. The oxidation potentials of DBMA and its HF-phase in acetonitrile differ by 0.87 V. The oxidation potentials of the respective protonated

compounds are substantially higher, they cannot be measured in acetonitrile, but there is no reason that the difference should become larger. Previous investigations of HF-phases of DBMA [17] and of aminoethers [18] respectively, gave some evidence for the structural element $-CF_3-CH_2-N-$, or even only CH_2 adjacent to CF_2, being almost resistant against electrochemical perfluorination. We think this hypothesis worth testing with defined substances, which are submitted to ECF, but we could not get such substances till now.

(2) As for the most important question concerning ECF mechanism, whether the fluorination reaction starts with the anodic oxidation of the organic compound or with the formation of a fluorinating agent, the results presented here favour the second way, i.e. the formation of 'active fluorine' is the decisive step. Obviously, the oxidation potential of the organic compound, the dibutylmethylamine, is of no importance for the electrofluorination process. Investigations of the primary products of aminoether ECF [18] have also favoured a radical attack as the primary one.

The nature of the 'active fluorine' formed at the anode is not yet known. Since nickel fluorides are very likely to play an important role in ECF, a kind of complex between nickel fluoride and fluorine, probably as atomic fluorine, can be assumed as the fluorinating agent. If there is not enough material to be fluorinated, fluorine will be set free, causing explosions.

EXPERIMENTAL

The electrochemical fluorination of dibutylmethylamine and the isolation of its 'HF-phase' and of the perfluorinated product was described elsewhere [16].

Voltammetric investigations in acetonitrile

The measurements were carried out in a 15 ml glass cell. Working electrode: Pt-(or Ni-)disk, made from a Pt (or Ni) wire pressed in PTFE, 3.14×10^{-2} cm^2 surface area, rotating with 3000 rpm (Pt). Reference electrode: Hg/Hg_2Cl_2/sat. KCl, connected via an agar-agar bridge and a Gaber-Luggin-capillary, which is 0.15

cm distant from the working electrode. Auxiliary electrode: Pt-wire (separated by a glass fritte). Working medium: acetonitril (distilled: 3 times over P_4O_{10}, 2 times over CaH_2) with 0.1 n $(Bu)_4NBF_4$ (2 times recrystallized from alcohol).

Voltammetric investigations in HF

The cell was manufactured from polyethylene, it has a volume of 50 ml. Working electrode: Ni-disk in PTFE, 3.14×10^{-2} cm² surface. Counter electrode: Ni-sheet, 15 cm² surface, 0.5 cm distant from the working electrode. Measurements were carried out applying the 2-electrodes-scheme.

For all investigations a polarograph PA-2 (ČSSR) was used with a potential sweep of 0.02 V/sec (rotating Pt) or 0.2 V/sec, respectively.

Additional experiments were carried out in a small, analytical ECF cell with a volume of 10 ml HF. The cell was completely manufactured from PTFE, it has one Ni-anode and one Fe-cathode (each 19 x 10 x 1 mm³) in a distance of 15 mm, and a Pt-wire as reference electrode. Measurements of the anodic potential vs. Pt were carried out with AHF, NaF/AHF, as well as with different solutions of DBMA HCl in HF by applying an increasing voltage between anode and cathode. Details of the HF solutions tested and the results are given in Fig. 2.

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