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Binary systems in electrochemical fluorination. I. Sulfamoyl fluoride and hydrazinium(2^+) fluoride

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Abstract

The effect on the formation of NF_3 of H_2NSO_2F added during the molten-salt electrolysis of ammonium hydrogen fluoride, was studied with varying amounts of hydrogen fluoride. Depending on the conditions of the reaction, the molten fluoride system not only served as solvent and fluorine source for the electrochemical fluorination (ECF) of H_2NSO_2F, but also as electrolyte. The main products were SO_2F_2, NF_3, N_2 and traces of N_2F_2. Results from similar experiments with $N_2H_6F_2$ are described.

Introduction

The use of simple inorganic substances as starting materials for electrochemical fluorination (ECF) generally results in degradation of the molecules and the formation of stable fluorine-free or fluorinated gaseous compounds [1, 2]. Thus, for the production of nitrogen trifluoride, the best method, apart from the direct fluorination of NH_3, is that of molten-salt electrolysis of ammonium fluoride–hydrogen fluoride systems [3]. The maximum current efficiency for NF_3 is approximately 70% with N_2 as the principal byproduct. In our attempt to improve this method, our initial idea was to replace the ammonium ion as the source of nitrogen by a simple carbon-free (to prevent formation of CF_4) compound containing only hydrogen, fluorine, and nitrogen in a more positive oxidation state than in NH_4^+. Our experiments with the only feasible compound, hydrazinium(2^+) difluoride, confirmed the poor performance found in earlier studies [4, 5] and also shed some light on the mechanism of the reaction. We then switched to compounds added to molten fluoride systems that were expected to give both NF_3 in good yields and a second useful product, thus increasing the overall value of the method. From sulfamoyl fluoride we expected SO_2F_2 and NF_3 without the formation of OF_2, which is often an unwanted impurity when using sulfur- and oxygen-containing compounds as starting materials for ECF [1, 6, 7].

Results and discussion

$N_2H_6F_2$

The molten-salt electrofluorination of $N_2H_6F_2$ in different NH_4F/HF systems was studied using nickel as electrode material. On monitoring the N_2H_4

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and NH_3 content during electrolysis, a contrary progression in their concentrations was observed. With N_2 and H_2 as the only gaseous products, the N_2H_4 concentration decreased steadily while that of NH_3 (remaining in the electrolyte as NH_4^+) increased. Not until most of the $N_2H_6F_2$ had vanished did the NF_3 production start and the electrolyte behave like a normal NH_4F/HF system.

In order to verify the formation of NH_3 from N_2H_4, as explained above, mixtures of $N_2H_6F_2$ and HF were electrolysed at approximately 120 °C. The results are shown in Fig. 1. Again, only insignificant amounts of NF_3 appeared in the electrolysis gas while the electrolyte still contained N_2H_4. However, the amount of NF_3 created up to this point was far too small to be attributed to formation from N_2H_4, again indicating NH_4^+ to be the source for NF_3 production.

Assuming that no NF_3 is derived from $N_2H_6F_2$, one can discuss two different reactions for the hydrazinium salt:

$$3N_2H_4 \longrightarrow 4NH_3 + N_2 \tag{1}$$

$$N_2H_4 \longrightarrow N_2 + 4H^+ + 4e^- \text{ anode reaction} \tag{2}$$

Taking into account all the experimental data, such as volume of gas produced, charge transported, electrolyte composition, etc., we found that the electrochemical oxidation of hydrazine [eqn.(2)] contributes approximately 57%, leaving 43% for the disproportionation [eqn.(1)].

No significant decomposition took place when similar mixtures of $N_2H_6F_2$ and $(HF)_x$ were kept at 110 to 125 °C for 5 days and for an additional 5

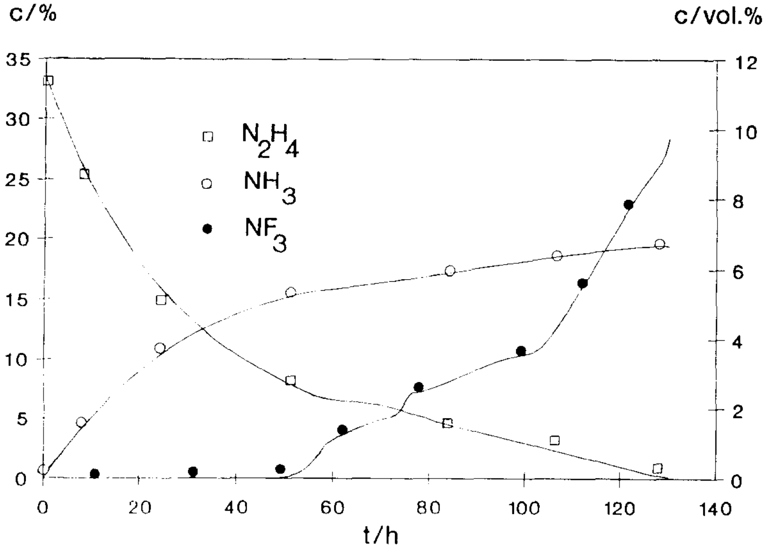

Fig. 1. Electrolysis of $N_2H_6F_2$/HF: changes in electrolyte composition and NF_3 production. For the sake of clarity, only a small number of symbols representing data points are shown.

days with nickel electrodes in contact with the molten electrolyte (final NH_3 concentrations $\leqslant 0.5\%$). Therefore, a catalytic decomposition or disproportionation of hydrazine [8] induced by the electrode or cell material (stainless steel) seems unlikely in the actual electrolysis.

H_2NSO_2F in KH_2F_3 and $(HF)_x$

Before applying H_2NSO_2F in molten ammonium fluoride, electrofluorination experiments were undertaken in KH_2F_3 and anhydrous HF. In this way, the only source of nitrogen was H_2NSO_2F itself and there could be no doubt about the origin of NF_3. The results are summarized in Table 1 using eqn.(3) for the calculation of the current efficiency.

$$H_2NSO_2F + 4HF \xrightarrow{6\ F} SO_2F_2 + NF_3 + 3H_2 \tag{3}$$

Yields for SO_2F_2 were highest in the KF/HF system. Since only small amounts of NF_3 were produced and the anode gas contained large amounts of N_2, the reaction is best described as follows:

$$H_2NSO_2F + HF \xrightarrow{3\ F} SO_2F_2 + 0.5N_2 + 1.5H_2 \tag{4}$$

The current efficiency for SO_2F_2 calculated following eqn.(4) is thus half that of eqn.(3). In $(HF)_x$, however, good yields for both NF_3 and SO_2F_2 can be achieved [based on eqn.(3)]. As shown by the immediate increase in current after adding H_2NSO_2F to $(HF)_x$, the dissolution takes place with protonation, possibly at the nitrogen atom. The higher yield of NF_3 in $(HF)_x$ can be explained by the difference in basicity of the molten-salt electrolytes and $(HF)_x$ respectively. A protonated H_2NSO_2F molecule will align in the electric field between the electrodes with its positive end pointing towards the cathode. Direct oxidation to nitrogen instead of stepwise fluorination to NF_3 should therefore be hindered in $(HF)_x$ because of its higher acidity.

^{19}F NMR experiments were performed at 0 °C to reveal the pathway of fluorination. Samples taken during ECF in HF were studied. No signals derived from F_2NSO_2F or $FHNSO_2F$ were detected. Chemical shifts for the known partly-fluorinated nitrogen–hydrogen species [9] also did not match with the observed signals. The only signals assigned so far are for SO_2F_2 and SF_6. These results conform to the fluorination of an adsorbed species.

TABLE 1

Current efficiencies obtained in the ECF of H_2NSO_2F using various electrolyte systems

Electrolyte system	Temp. (°C)	Starting conc. H_2NSO_2F (%)	Formal current efficiency		N_2 in anode gas (vol.%)
			NF_3 (5)	SO_2F_2 (%)	
KF/2HF	72–74	1–2.4	2–15	92–158	10–15
$HF_{liq.}$	0	6.0	44	104	4–10

H_2NSO_2F in NH_4HF_2/HF

Table 2 summarizes the results obtained in the various experiments. The amount of HF was varied in order to achieve different melting points and acidities of the electrolytes. Variations in temperature were limited since electrolyte temperatures much above the melting point of the respective system caused an unwanted increase in the HF vapour pressure above the electrolyte [10, 11]. The reason for the low yields in the case of NH_4HF_2 is not yet clear, but there is spectroscopic evidence that H_2NSO_2F decomposes at higher temperatures. The electrolytes with an HF ratio higher than 1.54 gave rise to frequent explosions. Consequently, subsequent experiments concentrated on $NH_4F + 1.54HF$.

Two kinds of electrolyses were performed with this system. When adding sulfamoyl fluoride in batches, the NF_3 concentration decreased while that for N_2 and SO_2F_2 increased. This indicates that fluorination of H_2NSO_2F is the preferred electrode reaction and that the H_2N group is oxidized mainly to nitrogen. A typical sequence is illustrated in Fig. 2.

Taking eqn.(3) to calculate the minimum amount of H_2NSO_2F that can be fluorinated within a given time, liquid sulfamoyl fluoride was then introduced continuously using a metering pump. The amount injected was kept close to that calculated under the assumption that no major changes in current would take place after starting pumping. Figure 3 shows that changes in current occurred and lead to the wave form of the graph. These fluctuations in current were partly due to the continual decrease of the effective electrode area caused by the consumption of the electrolyte and resulting problems in adjusting the metering pump. The current efficiencies obtained were 50 and 60% for NF_3 and SO_2F_2, respectively [eqn.(5) (see Table 2) and eqn.(4) respectively].

TABLE 2

Current efficiencies obtained in molten-salt electrochemical fluorination of H_2NSO_2F in various NH_3/HF systems

Electrolyte system	Temp. (°C)	Starting conc. H_2NSO_2F (%)	Formal current efficiency		N_2 in anode gas (vol.%)
			NF_3[a] (%)	SO_2F_2[b] (%)	
NH_4F/HF	125	2.9	36 (30)[c]	14	10–21
NH_4F/1.54HF	100	6.1	42 (64)	45	8–11
NH_4F/1.77HF	80	7.0	25 (50)	47	6–12
NH_4F/1.98HF	60	5.6	14 (9)	45	9–17

[a] Based on:

$$NH_3 + 6HF \xrightarrow{6\ F} NF_3 + 3H_2 \tag{5}$$

[b] Based on eqn.(4)

[c] Values in brackets: current efficiency without H_2NSO_2F.

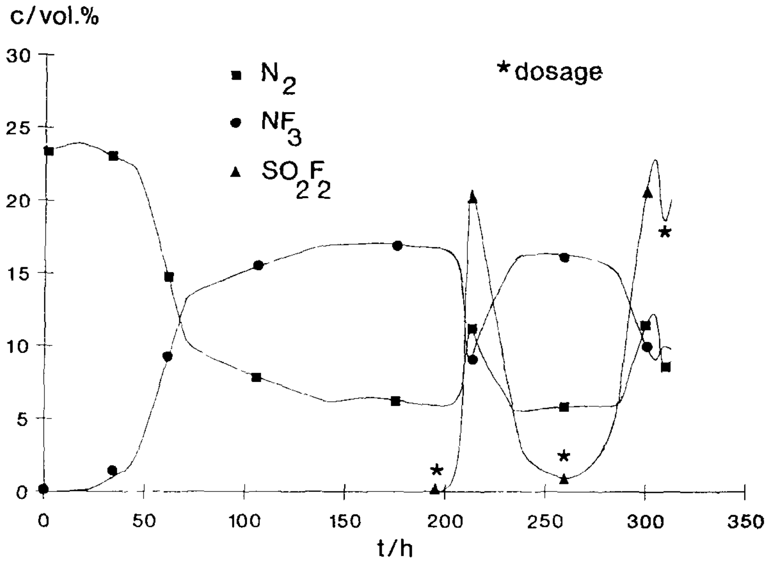

Fig. 2. Electrolysis of $NH_3/HF/H_2NSO_2F$ with batchwise dosage of sulfamoyl fluoride: changes in gas composition. For the sake of clarity, only a small of symbols representing data points are shown.

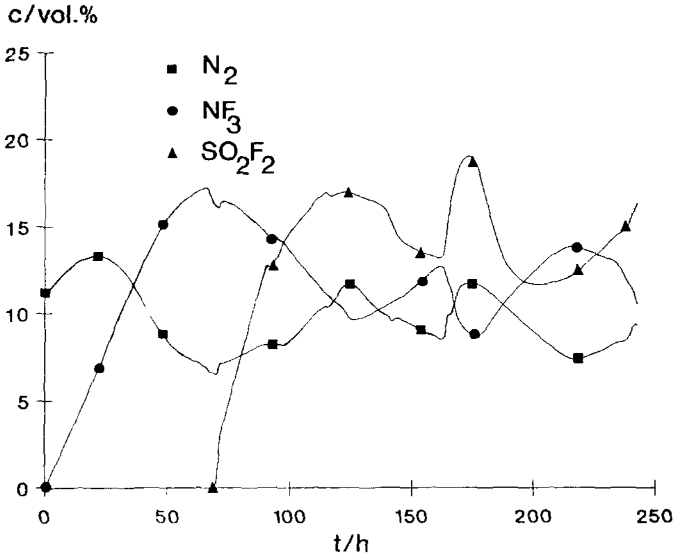

Fig. 3. Electrolysis of $NH_3/HF/H_2NSO_2F$ with continuous dosage of sulfamoyl fluoride: changes in gas composition. For the sake of clarity, only a small number of symbols representing data points are shown.

The only way to prove that NH_4^+ is the source of nitrogen for NF_3 is through the use of ^{15}N-enriched H_2NSO_2F or NH_4HF_2. Nevertheless, all the results strongly indicate that in the electrolysis of $NH_4F/HF/H_2NSO_2F$ mixtures with a deficiency of sulfamoyl fluoride, both compounds are electrofluorinated at the same time, yielding NF_3 from NH_4^+ and SO_2F_2 from H_2NSO_2F.

The ECF of sulfamoyl fluoride ran smoothly and selectively. SO_2F_2, N_2 and NF_3 were the main products. Traces of SF_6, SO_2, SOF_2 and N_2F_2 were sometimes detected. Small amounts of OF_2 were only found at the beginning of ECF in $(HF)_x$. Assuming that some water was still present in $(HF)_x$ when adding H_2NSO_2F, the following reaction [eqn. (6)] could have taken place.

$$H_2NSO_2F + H_2O \longrightarrow H_2NSO_3H + HF \tag{6}$$

Sulfamic acid is known to produce OF_2 under ECF conditions [1] and this could explain the presence of OF_2 in the electrolysis gas. The comparison with the ECF of $(H_2N)_2SO_2$ is worth noting. Engelbrecht *et al.* [1] observed high amounts of OF_2 when performing electrolysis in $(HF)_x$ and lower amounts in the KF/HF system. Again the difference in acidity of the two systems might serve as an explanation. An electrophilic attack of H_2F^+ at the oxygen atom and consequent synthesis of OF_2 is more likely in $(HF)_x$. Substitution of one NH_2 group by F must therefore lead to a decrease of basicity at the oxygen atom.

The use of sulfamoyl fluoride also gave some insight into the possible chemical behaviour of the terminal sulfuryl amide groups of an alkanedisulfonylamide under ECF conditions.

Experimental

Mixtures of NH_4HF_2 or KHF_2 with HF were made by condensing the required amount of HF onto the salts. Sulfamoyl fluoride was produced in high yields from commercially available $ClSO_2NCO$, which was first reacted with SbF_3 to give FSO_2NCO [12] and then hydrolysed [13]. $N_2H_6F_2$ was obtained from the reaction of hydrazine hydrate with hydrofluoric acid [14].

The type of cell used for ECF in AHF has been described earlier [15]. The cell for molten-salt electrofluorination was of similar construction except for the absence of a bottom outlet valve and an HF condenser. Cylindrical electrodes in place of an electrode pack of nickel plates were attached to the lid in an electrically insulated fashion. The outlets of the cells were connected with FEP tubing to two FEP-adsorber tubes filled with NaF. From there, the gas stream passed through a bubble counter and a wet gas meter. A device to take samples for infrared spectra and gas chromatography was located behind the two adsorber tubes. The current supplied by a direct current generator was recorded by a d.c. coulometer. The potential difference measured across the electrode connections on top of the cell was kept constant during electrolysis, allowing the current to change according to the conductivity of the electrolyte.

NMR spectra were taken on a Varian EM 360 L (56.45 MHz) and a Bruker WP 80 SY spectrometer (75.39 MHz) with CCl_3F as external standard. The analysis of the electrolysis gas was performed with an FTIR spectrometer (Nicolet 20 DXB) and a Fisher Model 1200 gas partitioner [conditions: 6.5′×1.8″ Porapak Q (80 to 100 mesh) and 11′×3/16″ molecular sieve 5 Å (45 to 60 mesh) in a dual-column, dual-detector (TCD) arrangement; carrier gas, helium (2 kg/cm^2); oven temperature 50 °C; bridge current 225 mA].

Conclusions

It was not possible to increase the current efficiency for NF_3 in the ECF of $N_2H_6F_2$ and H_2NSO_2F using different electrolyte systems. $H_2NSO_2F/NH_4F/HF$ served as a binary electrolyte, since it was possible to produce SO_2F_2 from H_2NSO_2F and NF_3 from NH_4^+ simultaneously. High yields of SO_2F_2 from H_2NSO_2F were obtained in KH_2F_3, which could therefore be used as a simple method for the production of SO_2F_2.

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