Journal of Fluorine Chemistry, 27 (1985) 23–33

Received: April 19, 1984; accepted: October 4, 1984

ELECTROCHEMICAL FLUORINATION OF ACETAMIDE AND FORMAMIDE IN MOLTEN KH_2F_3

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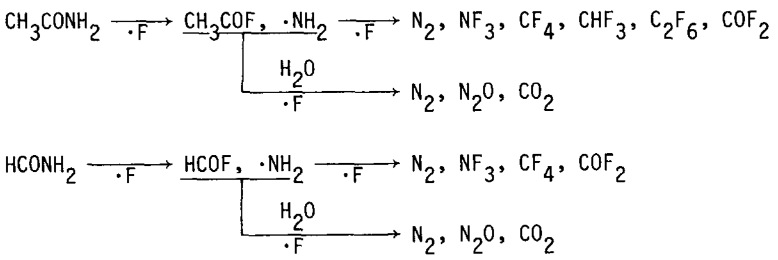
SUMMARY

The electrofluorination of acetamide (CH_3CONH_2) and formamide ($HCONH_2$) on the anode was studied in molten KH_2F_3 at 120°C. Amorphous carbon was used as the anode and Pt-rod as the reference electrode. Anodic products were analyzed by both gas chromatography and infrared spectroscopy.

In the cases of both CH_3CONH_2 and $HCONH_2$, the anode effect occurred often in electrolysis at the current density range of $3 \sim 20$ $mA{\cdot}cm^{-2}$ and the anode gas was then composed of $N_2(+O_2)$, NF_3, CF_4, C_2F_6, N_2O, $CO_2(+COF_2)$ and so on. The addition of 1.0 wt% LiF into the electrolyte decreased the yield of NF_3.

From these results, it is suggested that CH_3CONH_2 and $HCONH_2$ would react chemically with atomic fluorine produced on the $(C_XF)n$ $[x > 2]$ film by the discharge of fluoride ion. The mechanism of electrofluorination of CH_3CONH_2 or $HCONH_2$ in this melt is as follows;



0022-1139/85/$3.30

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INTRODUCTION

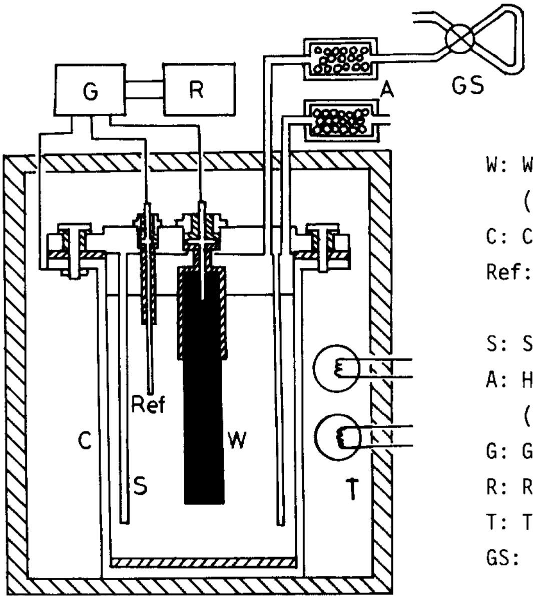
Nitrogen trifluoride (NF_3) is a stable gas at room temperature and has a strong oxidising action at higher temperatures [1]. Therefore, it has been already used as an oxidising agent for rocket fuels and a stable fluorinating agent [2 – 8]. It may be also used as a welding agent for metals and a gas filler in order to increase the life and the brightness of lamps [9]. Recently, a few researches have been attempted to develop the use of NF_3 as a laser gas [10– 12] and an etchant gas for a dry etching process [13– 16].

In an earlier paper on the electrolytic production of NF_3 from NH_4F (NH_3) or urea [$(NH_2)_2CO$] in molten KH_2F_3 [17], it was shown that the yield and the current efficiency of NF_3 are dependent upon both the current density and the concentration of starting material and that NH_4F (NH_3) is the best starting material from the view point of the current efficiency of NF_3. On the other hand, NF_3 was detected in the anode gas after only about ten hours from the start of electrolysis in the molten KH_2F_3 - $(NH_2)_2CO$ system, despite the fact that H_2O in the melt interferes with the electrofluorination of NH_4F (NH_3) [18–20]. It was concluded that the N-F compound can be obtained from RNH_2 (amine or amide) more easily than from NH_3.

In the present paper, the yield of each of the anodic products and the mechanism of anodic reaction have been discussed when amorphous carbon was used as the anode in the molten KH_2F_3 - acetamide or formamide systems.

EXPERIMENTAL

All the electrolytic cells of 1.0 or 1.5 dm^3 in capacity were made of steel [21] as shown in Fig. 1. The anode holders were designed for the airtight seal of the cell [20]. Two types of amorphous carbon rods (diameter of 16 mm, length of 1 cm and surface area of 2 cm^2 for determination of polarization curves; diameter of 32 mm, length of 10 cm and surface area of $80 \sim 100$ cm^2 for electrolytic fluorination), the inside wall of the cell and a platinum wire were used as anode, cathode and reference electrode, respectively. The inside of the cell bottom was masked by polytetrafluoroethylene resin and the anode compartment of the cell was separated from the cathode compartment by a skirt of steel welded to the cell cover. The anode gas was passed through the absorption tube of gasous HF filled with tablets of sodium fluoride (NaF) and then led to a gas-sampler. The sample gas was



W: Working electrode
(Amorphous carbon)
C: Counter electrode
Ref: Reference electrode
(Pt wire)
S: Skirt
A: HF absorber
(NaF pellets)
G: Galvanostat
R: Recorder
T: Thermostatic box
GS: Gas sampler

Fig. 1. Experimental apparatus for electrofluorination.

fractionated by gas chromatography and the fractionated samples, each corresponding to a distinct peak on the gas chromatogram, were identified by infrared spectroscopy.

After the starting material was added to the molten KH_2F_3, the electrolyte was pre-electrolyzed at a low current density until NF_3 was detected, and then anodic polarization curves were determined by cyclic voltammetry.

RESULTS

Effect of current density and concentration of CH_3CONH_2 or $HCONH_2$ on each yield of anodic products

In the presence of the considerable amount of H_2O in the electrolyte, nitrogen trifluoride (NF_3) was first evolved in the anode gas after a few days or a week from the start of electrolysis in the molten KH_2F_3 - NH_4F system [17]. Hence, pre-electrolysis is also necessary for the removal of H_2O in the electrolyte in the electrolytic preparation of NF_3.

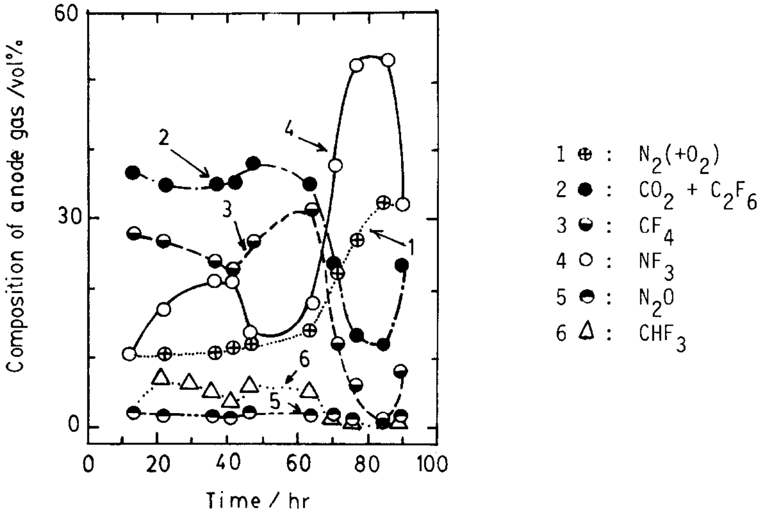


Fig. 2. Change of anode gas composition as a function of time.
Conditions: 2.5 mol% CH_3CONH_2, 5.4 $mA \cdot cm^{-2}$, 3.7∼5.2 V *vs.* Pt.

Fig. 2 shows the change of anode gas composition in electrolysis at 2.5 mol% CH_3CONH_2 and 5.4 $mA \cdot cm^{-2}$ as a function of time. At the start of electrolysis, carbon dioxide (CO_2), hexafluoroethane (C_2F_6) and tetrafluoromethane (CF_4) were main products. In spite of no pre-electrolysis, NF_3 was detected in the anode gas after electrolysis for 10 hours and its composition ratio of anode gas, *i.e.* yield, increased with the decrease of the composition ratios of CO_2, C_2F_6 and CF_4 to reach the maximum value of 53 %. The total amount of anode gas can be calculated from the following reactions of equations (1) to (8).

$$2(-NH_2) + 4F^- \longrightarrow N_2 + 4HF + 4e^- \qquad (1)$$

$$-NH_2 + 5F^- \longrightarrow NF_3 + 2HF + 5e^- \qquad (2)$$

$$2(-NH_2) + H_2O + 6F^- \longrightarrow N_2O + 6HF + 6e^- \qquad (3)$$

$$H_3C- + 5F^- \longrightarrow CHF_3 + 2HF + 5e^- \qquad (4)$$

$$H_3C- + 7F^- \longrightarrow CF_4 + 3HF + 7e^- \qquad (5)$$

$$2(H_3C-) + 12F^- \longrightarrow C_2F_6 + 6HF + 12e^- \qquad (6)$$

$$=CO + 2F^- \longrightarrow COF_2 + 2e^- \qquad (7)$$

$$COF_2 + H_2O \longrightarrow CO_2 + 2HF \qquad (8)$$

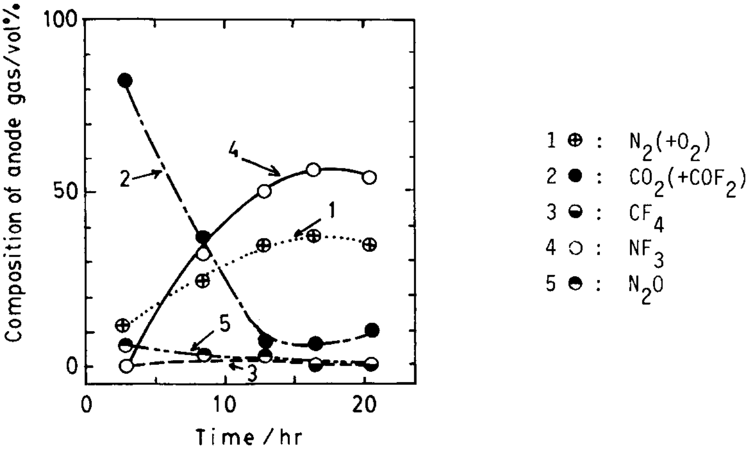


Fig. 3. Change of anode gas composition as a function of time.
Conditions: 4.0 mol% $HCONH_2$, 5.3 $mA{\cdot}cm^{-2}$, 2.0∿5.2 V vs. Pt.

The yield of each anodic product under various electrolytic conditions is given in Table 1. The yield was represented as the ratio of the integrated amount of each product generated during electrolysis to the total amount of all compounds in the anode gas on the basis of Fig. 2. The best yield of NF_3 in this system was obtained in the case of 2.5 mol% CH_3CONH_2 and the current density of 5.4 $mA{\cdot}cm^{-2}$. The addition of 1.0 wt% LiF into the electrolyte, however, decreased the yield of NF_3. The yield of CF_4 was also decreased in the presence of colloidal LiF in the electrolyte.

Fig. 3 shows the change of anode gas composition in electrolysis at 4.0 mol% $HCONH_2$ and 5.3 $mA{\cdot}cm^{-2}$ as a function of time. At the start of electrolysis, CO_2 was also the main product in this system and its amount decreased with the lapse of time. NF_3 was detected in the anode gas after electrolysis for only 3 hours without pre-electrolysis and its composition ratio of anode gas increased with the decrease in the amount of CO_2. This fact indicates that H_2O in the electrolyte was more easily eliminated by the formation of CO_2 according to the equation (8).

The effect of the electrolytic condition on the yield of each anodic product in the case of $HCONH_2$ is given in Table 2. The best yield of NF_3 was obtained in the case of 4.0 mol% $HCONH_2$ and the current density of 5.3 $mA{\cdot}cm^{-2}$. The addition of 1.0 wt% LiF into the electrolyte also decreased the yield of NF_3. But, the yield of CF_4 was always below only 1.8 % of anode gas, so that CF_4 will be mainly produced from the decomposition of $(C_xF)n$ and /or (CF)n films in this system.

TABLE 1

Effect of CH_3CONH_2-concentration, added LiF and current density on the yield of each product in the anode gas

LiF (wt%)	CH_3CONH_2 (mol%)	C.D.* ($mA \cdot cm^{-2}$)	D.E.* (h)	Q.E.* (C)
no addition	0.4	5.9	29.6	47,900
	2.5	3.3	198	214,000
	2.5	5.4	89.7	161,000
1.0	2.5	5.7	95.7	172,000
1.0	2.5	20.4	41.1	236,000

Yield of products in anode gas (%)

$N_2(+O_2)$	CF_4	NF_3	$CO_2(+COF_2)$	N_2O	C_2F_6	CHF_3	Unknown substance
77.7	5.1	2.8	12.0	0.2	trace	1.7	0.5
56.4	11.9	12.0	16.4	1.0	trace	1.5	0.9
18.1	19.1	26.5	29.4	1.4	0.3	3.0	1.4
56.3	10.4	6.3	20.4	0.7	0.3	1.8	trace
61.2	7.3	7.1	21.1	1.0	trace	0.9	0.8

*C.D.: Current Density; D.E.: Duration of Electrolysis;
Q.E.: Quantity of Electricity.

TABLE 2

Effect of $HCONH_2$-concentration, added LiF and current density on the yield of each product in the anode gas

LiF (wt%)	$HCONH_2$ (mol%)	C.D.* ($mA \cdot cm^{-2}$)	D.E.* (h)	Q.E.* (C)
no addition	1.0	5.5	12.8	21,200
	2.3	4.9	25.0	54,900
	2.5	11.0	28.3	87,600
	4.0	5.3	20.6	33,600
	8.0	5.5	32.9	55,500
1.0	2.5	5.4	19.2	31,400

Yield of products in anode gas (%)

$N_2(+O_2)$	CF_4	NF_3	$CO_2(+COF_2)$	N_2O	Unknown substance
67.1	0.46	23.0	7.91	1.50	trace
45.0	0.28	23.7	29.1	1.97	trace
70.2	0.22	12.4	9.20	0.98	trace
33.3	1.02	36.7	26.3	2.60	trace
60.5	0.19	11.3	19.5	8.51	trace
48.3	0.15	7.98	42.1	1.50	trace

*C.D.: Current Density; D.E.: Duration of Electrolysis;
Q.E.: Quantity of Electricity.

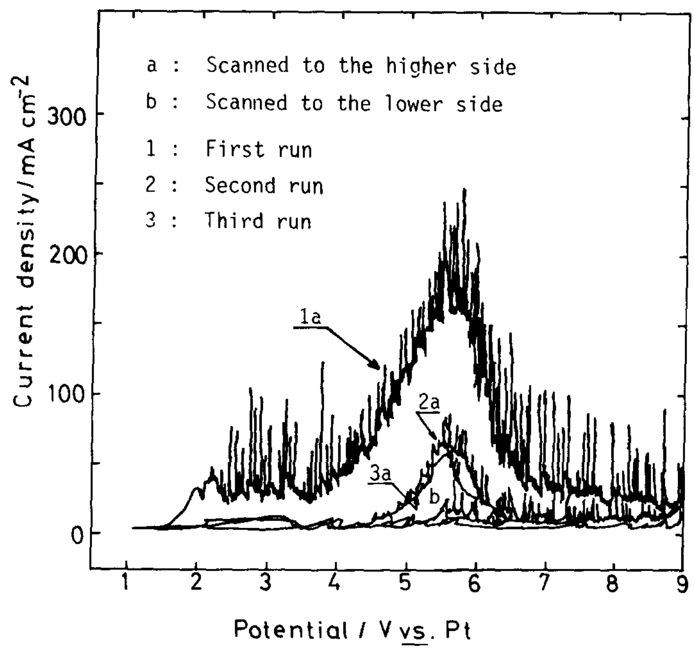


Fig. 4. Cyclic voltammograms in KH_2F_3 - 2.5 mol% CH_3CONH_2 system with scan rate of 1/60 $V{\cdot}s^{-1}$.

Anodic polarization curve

As the surface of the carbon electrode was covered with the carbon fluoride film in polarization, it was very difficult to analyze each effect of the current density, the anode potential and the concentration of CH_3CONH_2 or $HCONH_2$ on yields of each anodic products from the anodic polarization curve determined by only a stationary method; i.e. galvanostatic or potentiostatic method. Hence, anodic polarization curves determined by the cyclic voltammetry in a molten KH_2F_3 - CH_3CONH_2 system and a molten KH_2F_3 - $HCONH_2$ system are shown in Fig. 4 and Fig. 5, respectively.

The cyclic voltammograms of the second run (curves 2) and the third run (curves 3) in Figs. 4 and 5 were different from that of the first run (curves 1). This fact indicates that the surface of the carbon electrode is converted from the original carbon surface to a $(C_xF)n$ [X > 2] surface [17] by the anodic polarization. This compound, $(C_xF)n$ is an electroconductible film of carbon fluoride and its surface energy is lower than that of carbon [17]. In anodic scan, the anodic current density at these potentials lower than 7 V on curves 1 was very large, so that CH_3CONH_2 or $HCONH_2$ would

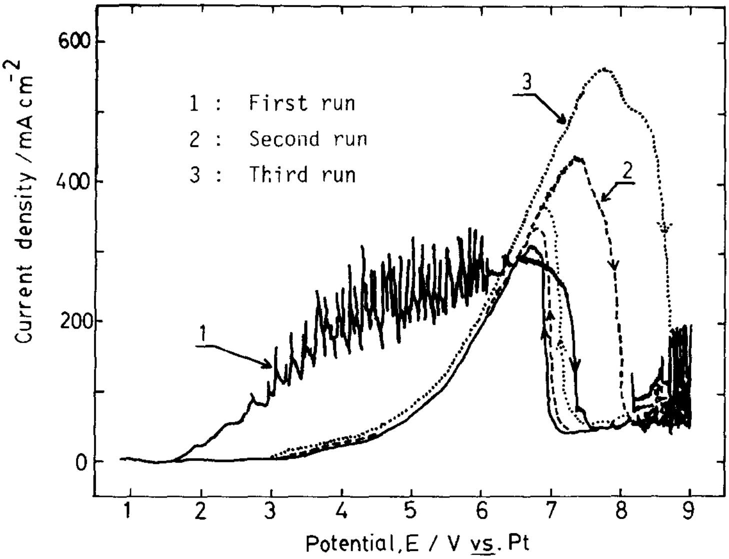


Fig. 5. Cyclic voltammograms in KH_2F_3 - 2.5 mol% $HCONH_2$ system with scan rate of 1/20 V·s^{-1}.

be directly discharged on the bare carbon to form N_2, CO, CO_2, C_2H_6 and so on. But, at the same potentials, the anodic current density observed in curves 2 and 3 was much smaller than that in curves 1, so that neither CH_3CONH_2 nor $HCONH_2$ would be discharged on the $(C_xF)n$ film and these amides would be mainly fluorinated by atomic fluorine formed through the discharge of fluoride ion on this film. The phenomenon of the breakdown of current at the potentials between 6 and 7 V is called the anode effect and may be due to development of a (CF)n film from $(C_xF)n$.

When the anode potential was scanned to the lower side from 9 V, a maximum positive current was observed at anode potentials of 6∿7 V. It is supposed that the (CF)n film on the carbon anode was activated by only the disproportionation reaction (eq. 9) as shown in Fig. 4 and by both the disproportionation reaction and the reduction of its film with $HCONH_2$ (eq. 10) as shown in Fig. 5, and finally, the new carbon surface was changed again to the $(C_xF)n$ film by the following reaction (eq. 11).

$$(CF)n \longrightarrow C^*,\ CF_4,\ C_2F_6 \qquad (9)$$

$$(CF)n + HCONH_2 \longrightarrow C^*,\ FCONH_2 \qquad (10)$$

$$mC^* + nF^- \longrightarrow (C_xF)n + ne^- \qquad (11)$$

The surface energy of (CF)n film is only 6 ± 3 ergs·cm^{-2} [22] and so the electrode surface does not come into contact with the solution.

DISCUSSION

From the obtained results, the mechanism of the electrofluorination of CH_3CONH_2 or $HCONH_2$ may be proposed as follows [17], [21], [23], [24]. At first, fluoride ion is discharged on the carbon electrode to form the $(C_xF)n$ film according to the equation (11'). On this film, only fluoride ion is discharged successively to produce atomic fluorine (eq. 12). In the absence of a fluorinated substance, it combines with another atomic fluorine to produce fluorine gas (eq. 13).

$$mC + nF^- \longrightarrow (C_xF)n + ne^- \qquad (11')$$

$$(C_xF)n + F^- \longrightarrow (C_xF)n\cdot F + e^- \qquad (12)$$

$$2(C_xF)n\cdot F \longrightarrow 2(C_xF)n + F_2 \qquad (13)$$

In the presence of CH_3CONH_2 or $HCONH_2$ in the electrolyte, atomic fluorine reacts with these starting materials and a few intermediates successively according to the equations (14–20) to produce some fluoro-compounds. In these cases, oxygen comes from both H_2O in the melt and carbonyl group in CH_3CONH_2 or $HCONH_2$.

$$CH_3CONH_2 \xrightarrow[\cdot F]{} CH_3COF,\ \cdot NH_2\ [\text{or } FNH_2] \qquad (14)$$

$$CH_3COF \xrightarrow[\cdot F]{-HF} CHF_3,\ CF_4,\ C_2F_6,\ COF_2 \qquad (15)$$

$$HCONH_2 \xrightarrow[\cdot F]{} HCOF,\ \cdot NH_2\ [\text{or } FNH_2],\ FCONH_2 \qquad (16)$$

$$HCOF \xrightarrow[\cdot F]{} COF_2 + HF \qquad (17)$$

$$FCONH_2 \longrightarrow COF_2,\ \cdot NH_2\ [\text{or } FNH_2] \qquad (18)$$

$$COF_2 + H_2O \longrightarrow CO_2 + 2HF \qquad (8)$$

$$\cdot NH_2\ [\text{or } FNH_2] \xrightarrow[\cdot F]{-HF} N_2,\ NF_3 \qquad (19)$$

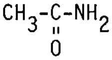
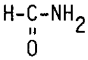
$$\cdot NH_2 \xrightarrow[\cdot F/H_2O]{} N_2,\ N_2O \qquad (20)$$

When atomic fluorine attacks CH_3CONH_2 or $HCONH_2$, it cleaves the weaker bond in each starting material and it combines with a fragment to form a fluoro-compound. Then, a binding partner with atomic fluorine may be mainly arranged according to the binding energies in each starting material and products as given in Table 3 [25].

Besides, NF_3 could be also obtained in electrofluorination of CH_3CONH_2 and $HCONH_2$ more easily than in that of NH_4F (or NH_3), as mentioned in electrofluorination of urea and dicyanodiamide [21], [23]. This result may be reasonably explained according to the binding energies in starting materials and products [21], [23], [24], [26].

TABLE 3

Binding energies of CH_3CONH_2, $HCONH_2$ and fluoro-compounds [25]

Starting material	Binding energy (kcal·mol^{-1})	Fluoro-compounds Binding energy (kcal·mol^{-1})
 $CH_3-\underset{\underset{O}{\|}}{C}-NH_2$	D(C=O) = 164∿175 D(C-C) = 88 D(C-N) = 70 D(HN-H) = 88 D(N-H) = 88 D(H_2C-H) = 106 D(HC-H) = 106 D(C-H) = 81	D(CH_3CO-F) = 118 D(H_3C-F) = 108 D(C-F) = 110∿120 D(FC-F) = 140 D(F_2C-F) = 91 D(F_3C-F) = 121 D(F_3C-H) = 103 D(F_3C-CF_3) = 69 D(N-F) = 78 D(FN-F) = 78 D(F_2N-F) = 62 D(H-F) = 135 D(F-F) = 37
 $H-\underset{\underset{O}{\|}}{C}-NH_2$	D(C=O) = 164∿175 D(C-N) = 70 D(HN-H) = 88 D(N-H) = 88 D(C-H) = 81	

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