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Electrochemical Fluorination of *N*-Nitrosodiethylamine[1]

Nobuatsu WATANABE, Masatake HARUTA, and Byongte CHANG
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto

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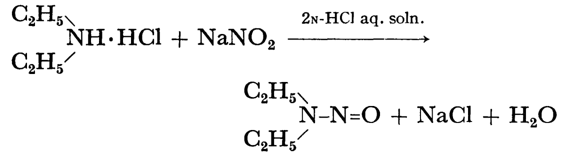
The fluorination of $(C_2H_5)_2N\text{-}NO$ at a nickel anode under a variety of operating conditions resulted in the formation of liquid products such as $(CF_3)_2C_2F_5N$, $(C_2F_5)_2CF_3N$, $(C_2F_5)_3N$, and the compounds containing C–N groups together with gaseous fragmentation products such as CF_4, C_2F_6, CHF_3, NF_3, and N_2. Current efficiency of total gaseous products increased appreciably as the concentration of substrate and current density became higher. Effect of electrolysis temperature was so characteristic as observed in the fluorination of triethylamine that there existed the temperature at which a maximum value of current efficiency was given. On the basis of both the experimental results on the effects of operating conditions and the electrochemical measurements in hydrogen fluoride solutions of $Et_2N\text{-}NO$, mechanism of the fluorination reaction was discussed and compared with those of diethylamine and triethylamine.

Our previous work on the electrochemical fluorination of *n*-propyl, diethyl and triethyl amines[2] has shown that these amines underwent not only substitution reaction of hydrogen for fluorine but also simultaneous fragmentation reaction of C–N and C–C bonds in the molecule, and that the fragmentation reaction was appreciably affected by various operating conditions. Since it is reasonably expected that these substitution and fragmentation reactions are subject to an influence of a substituent in an amine molecule as well as the operating conditions, $Et_2N\text{-}NO$ was chosen as a substrate to examine effect of *N*-nitroso group on the fluorination reaction. Many studies have been done on chemical or electrochemical fluorination of a series of representative amines, but no work on the fluorination of nitroso amine has yet been done. Effects of substrate concentration, electrolysis temperature and current density on the fluorination of $Et_2N\text{-}NO$ were investigated by means of the method reported previously.[2]

Experimental

Materials. $Et_2N\text{-}NO$ was prepared from diethylamine hydrochloride and sodium nitrite by the usual method.[3]



$$(C_2H_5)_2NH\cdot HCl + NaNO_2 \xrightarrow{2\text{N-HCl aq. soln.}} (C_2H_5)_2N\text{-}N{=}O + NaCl + H_2O$$

The prepared material was identified by its known infrared spectrum. The purity was checked up to be more than 99.5% by gas chromatography. The anhydrous hydrogen fluoride (purity 99.9%) was supplied by Daikin Co. Ltd.

Method. The apparatus and experimental methods used here were virtually identical with those described before.[2] The electrolytic cell used in the present study was an iron cylindrical vessel having a capacity of 700 m*l*, containing a pack of alternate nickel anodes and cathodes (99.9% in purity and 1 mm in thickness, effective anode area 3 dm^2). The liquid products collected in a dry ice–methanol trap were rectified in a low temperature precision still. Preparative separation of each fraction obtained by rectification was carried out with gas chromatography using Porapack R as column packing.

Results

Gaseous products. Results of the electrofluorination of *N*-nitrosodiethylamine under a variety of operating conditions are given in Table 1. $Et_2N\text{-}NO$ yielded C_2F_6, NF_3, CF_4, CHF_3, N_2, and CO_2 as principal gaseous products and relatively small amounts of imperfectly fluorinated CHF_2CF_3, CHF_2CHF_2, and CH_2F_2. The current efficiency of each product was calculated according to the equation based on a discharge of fluorine ion as follows.

$$F^- \longrightarrow F\cdot + e \tag{1}$$

$$\rangle N\text{-}NO + 2F\cdot \longrightarrow N_2 + OF_2 \tag{2}$$

$$\rangle N\text{-} + 3F\cdot \longrightarrow NF_3 \tag{3}$$

$$\rangle C\langle + 2H_2O + 4F\cdot \longrightarrow CO_2 + 4HF \tag{4}$$

$$\text{-}C_2H_5 + 13F\cdot \longrightarrow 2CF_4 + 5HF \tag{5}$$

$$\text{-}C_2H_5 + 11F\cdot \longrightarrow C_2F_6 + 5HF \tag{6}$$

$$\text{-}C_2H_5 + 9F\cdot \longrightarrow 2CHF_3 + 3HF \tag{7}$$

$$\text{-}C_2H_5 + 5F\cdot \longrightarrow 2CH_2F_2 + HF \tag{8}$$

$$\text{-}C_2H_5 + 9F\cdot \longrightarrow CHF_2CF_3 + 4HF \tag{9}$$

$$\text{-}C_2H_5 + 7F\cdot \longrightarrow CHF_2CHF_2 + 3HF \tag{10}$$

The products obtained were identified by their known infrared spectra[4] except for CHF_2CHF_2 and N_2. N_2 was identified by gas chromatography equipped with Molecular Sieve 5A. CHF_2CHF_2 was identified by infrared and mass spectra as its spectral data were not given in the literature. Its infrared spectrum shows a strong absorption band at 8.9 μ and its mass spectrum is shown in Table 2.

The current efficiency for F_2 and OF_2 evolution was 0.3—1.0% for 2.4 mol% solution and 0.7—1.5% for 0.3 mol% solution, which indicated a tendency to increase with decreasing concentration. The current efficiency for dissolution of nickel electrode, calculated from the weight change before and at the end of electrolysis assuming that nickel dissolved as Ni^{2+} ion,

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[1] Presented at the Annual Meeting of the Chemical Society of Japan, April, 1971.

[2] B. Chang, H. Yanase, K. Nakanishi, and N. Watanabe, *Electrochim. Acta*, **16**, 1179 (1971).

[3] A.H. Blatt, "Organic Syntheses", Coll. Vol. II, 1950, p. 211.

[4] J. H. Simons, "Fluorine Chemistry", Academic Press, New York, (1954), Vol. 2.

TABLE 1. OPERATING CONDITIONS FOR ELECTROCHEMICAL FLUORINATION OF Et_2N-NO

Concn. (mol%)	Temp. (°C)	C.d. (mA/cm²)	Cell voltage (V)	Current efficiency (%)									
				N_2	CF_4	NF_3	CO_2	C_2F_6	CHF_3	CH_2F_2	CHF_2CF_3	CHF_2CHF_2	Total
0.3	5±1	10	5.1	4.2	1.5	1.9	2.8	13.3	2.0	0.2	3.1	0.4	29.4
2.4	4±1	2	5.0	6.8	2.4	1.7	4.8	14.3	3.2	0.3	1.4	0.5	35.4
2.4	5±1	5	5.3	4.5	3.8	3.0	3.4	23.3	3.3	0.3	1.8	0.5	43.8
2.4	5±1	10	5.4	3.2	4.9	4.9	5.2	31.9	3.0	0.2	2.4	0.9	56.6
2.4	6±1	20	5.6	2.2	4.1	5.9	4.1	40.7	2.7	0.2	1.8	0.8	62.5
2.4	7±1	30	5.8	1.8	4.4	6.7	3.7	47.0	2.2	0.2	2.7	1.0	69.7
12.7	−25±2	20	6.9	3.4	5.1	7.0	2.2	51.8	1.0	—	1.6	0.9	73.0
12.7	−15±2	20	6.4	2.8	8.6	8.2	3.3	58.6	0.5	0.2	2.2	—	84.4
12.7	−2±2	20	5.9	3.2	9.1	8.4	4.3	58.5	1.6	—	1.7	0.2	87.0
12.7	9±1	20	5.6	3.4	8.6	8.2	4.7	57.6	1.6	—	2.5	0.6	87.2
12.7	19±2	20	5.5	3.9	8.2	6.7	4.9	45.6	2.0	—	2.4	0.5	74.2

TABLE 2. MASS SPECTRUM OF CHF_2CHF_2

m/e	Pattern coefficient	+Ion
51	100	CHF_2
83	44.3	CHF_2CHF
101	13.4	CHF_2CF_2
102	6.6	CHF_2CHF_2

amounted to 0.85%. This value is about three times as large as those in the fluorinations of diethylamine and triethylamine.

1) Effect of Substrate Concentration: In Fig. 1 are given the total current efficiencies of both anode and cathode gaseous products at three different concentrations 0.3, 2.4, and 12.7 mol% under the constant electrolysis temperature 5±1°C and current density 10 mA/cm². The current efficiency of total gases produced at the anode increases linearly with the logarithm of substrate concentration. The current efficiency for hydrogen evolution also increases with concentration but it does not exceed 40% at 0.3 mol%. Such a low value would be due to the recombination of hydrogen with fluorine which cannot be used for fluorination because of low concentration. On the assumption that the difference of current efficiency between gaseous anode products and hydrogen evolved at cathode is associated with the current efficiency of high boiling liquid products, it would be relatively advantageous to set up concentration around 2.5 mol% for the formation of liquid products less subject to the cleavage reaction. Figure 2 shows a trend that the molar formation ratios of imperfectly fluorinated CHF_2CF_3 and CHF_3 decrease with increasing concentration whereas those of C_2F_6, NF_3, and CF_4 increase. Molar ratio of NF_3 to N_2 is 0.31, 0.65, and 0.97 for 0.3, 2.4, and 12.7 mol% solution, respectively, which shows an increasing trend with concentration. Therefore, it is readily understood that concentration contributes to an acceleration of rate of fluorination. Molar ratio of C_2F_6 to NF_3 is about two, irrespective of substrate concentration, which is similar value as observed in the electrofluorination of diethylamine. The molar ratio of fluorinated ethanes C_2F_6, CHF_2CF_3, and CHF_2CHF_2 to fluorinated methanes CF_4, CHF_3, and CH_2F_2 increases with concentration; 2.18, 2.23, and 3.67 at 0.3, 2.4, and 12.7 mol%, respectively. This indicates that the higher the concentration is, the more readily C–N bonds are cleaved than C–C bonds.

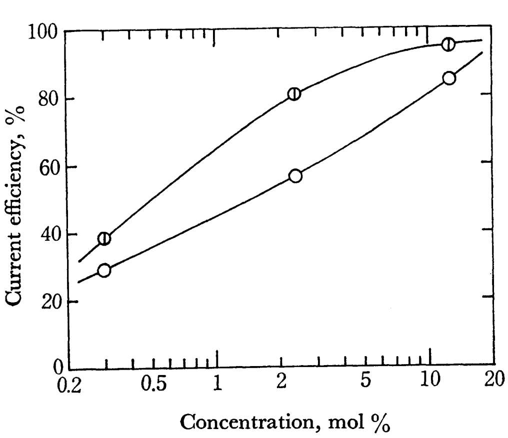

Fig. 1. Effect of concentration on the total current efficiency of gaseous products.
○: anode, ⦶: cathode temperature: 5±1°C current density: 10 mA/cm²

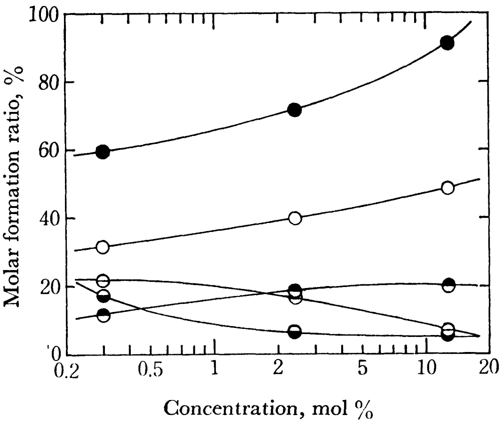

Fig. 2. Dependence of molar formation ratios of principal gaseous products on concentration.
●: C_2F_6, ○: NF_3, ◓: CF_4, ⊖: CHF_3, ◒: C_2HF_5
temperature: 5±1°C current density: 10 mA/cm²

2) Effect of Electrolysis Temperature: Figure 3 shows the effect of electrolysis temperature on the total current efficiency of gaseous products under constant concentration and current density. The total current efficiency increases rapidly in the range of −15—6°C at 2.4 mol%. On the other hand, there exists the tem-

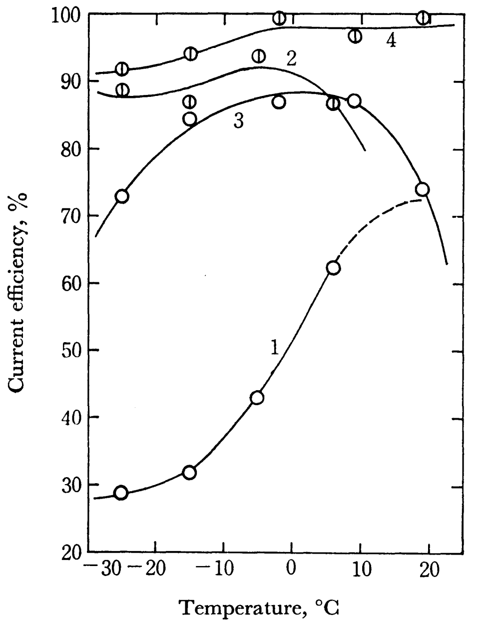

Fig. 3. Effect of temperature on the total current efficiency of gaseous products.
○: anode, ⦶: cathode current density: 20 mA/cm^2
1 and 2: 2.4 mol%, 3 and 4: 12.7 mol%

perature at which a maximum value of current efficiency is given at 12.7 mol%. It is obvious that the temperature dependence of current efficiency is not due to the recombination of fluorine with hydrogen, since the current efficiency of hydrogen evolution always exceeds 90%. The current efficiency of gaseous products for 12.7 mol% solution is always very high in the temperature range investigated and the maximum value reaches 87.2%, which implies that fragmentation takes place vigorously in the liquid phase. The relation is given in Fig. 4 between the current efficiencies of principal gaseous products and temperature for 2.4 mol% solution. The current efficiencies of NF_3 and CF_4 increased slightly while that of CHF_2CF_3 decreased slightly. An appreciable increase in the current efficiency was observed only for C_2F_6. It is also observed for 12.7 mol% solution that the current efficiency of C_2F_6 determines the temperature dependence of the total current efficiency of gaseous products. Since the molar formation ratios of CHF_3 and CHF_2-CF_3 decrease with temperature whereas that of C_2F_6 noticeably increases, it is evident that rate of fluorination is accelerated with increasing temperature. Figure 5 shows that molar ratio of C_2F_6 and CHF_2CF_3 to CF_4 and CHF_3 increases with temperature for 2.4 mol% solution, whereas it decreases for 12.7 mol% solution. As the boiling points of hexafluoroethane and pentafluoroethane are low compared with the electrolysis temperature, −78 and −23°C, respectively, it may scarecely occur that these fluorinated ethanes are subjected to further fluorination to yield fluorinated methanes. The fluorinated methanes may be produced from the scisson of C–C bonds before the breaking of C–N bonds occurs. Since most of the cleavage of C–C bonds would be thought to take place before C–N bonds are cleaved as stated above, the more readily C–N bonds are cleaved, the larger becomes the molar ratio of fluorinated ethanes to fluorinated methanes. Therefore, in order to restrain the breaking of C–N bonds, low concentration of Et_2N–NO and low temperature are prefered. But, if concentration is high, high temperature is prefered to low temperature.

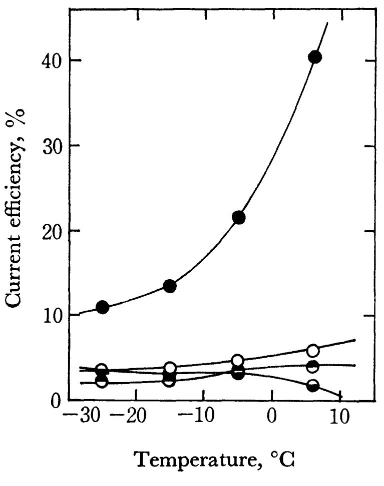

Fig. 4. Effect of temperature on the current efficiencies of principal gaseous products.
●: C_2F_6, ○: NF_3, ◓: CF_4, ◒: C_2HF_5
concentration: 2.4 mol% current density: 20 mA/cm^2

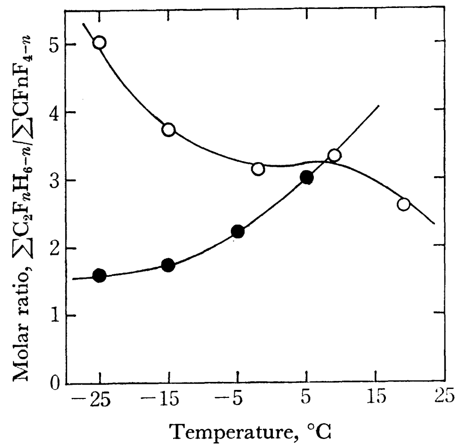

Fig. 5. Dependence of molar ratio of fluorinated ethanes to fluorinated methanes on temperature.
●: 2.4 mol%, ○: 12.7 mol%
current density: 20 mA/cm^2

In the case of Et_3N there existed the temperatures at which maximum values of current efficiency were given for both 2 and 10 mol% solutions, but only for 12.7 mol% solution in the case of Et_2N–NO. The fact that the temperature at the maximum value of current efficiency for 2 mol% solution of Et_3N was shifted to 7°C from −25°C for 10 mol% solution implies that the maximum value of current efficiency for 2.4 mol% solution of Et_2N–NO would be given at temperature higher than 15°C. Thus, it can also be concluded for the electrofluorination of Et_2N–NO that temperature has two opposing factors affecting the cleavage of bonds in a molecule: Solubilities of fluorinated products in HF solution is high at low temperature, and more likely to be exposed to further attack by fluorine. Low temperature makes, on the other hand, the fluorination reaction proceed mildly by taking away a large amount

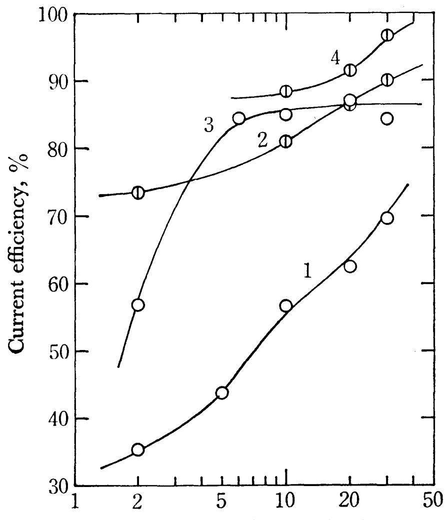

Fig. 6. Effect of current density on the total current efficiency of gaseous products.
○: anode, ⦶: cathode
1 and 2: 2.4 mol%, 3 and 4: 12.7 mol%
temperature: 7±2°C

of heat of reaction. At high temperature, the reverse is the case.

3) Effect of Current Density: Effect of current density on the total current efficiency of gaseous products is shown in Fig. 6. A remarkable increase in current efficiency is observed for 2.4 mol% solution, while for 12.7 mol% solution it comes up to such a high value as 85% after a remarkable increase in the range of 2—5 mA/cm². The current efficiency for hydrogen evolution also shows an upward tendency with current density. It was observed that the increase in total current efficiency was mainly due to an increase in that of C_2F_6. Therefore it is understood that cleavage of C–N bonds occurs as current density becomes higher. Figure 7 shows the dependence of molar formation ratios of principal gaseous products on current density. C–N bonds are more readily cleaved than C–C bonds as current density is increased, since the ratio of C_2F_6 and CHF_2CF_3 to CF_4 and CHF_3 increases with current density. A tendency was observed that molar formation ratios of C_2F_6 and NF_3 increased with current density, while those of CHF_3 and CHF_2CF_3 decreased. This tendency is due to the fact that an increase in current density leads to higher concentration of fluorine and then to an acceleration of fluorination rate. The acceleration of rate of fluorination by increasing current density is also evidenced by the change of molar ratio of NF_3 to N_2; 0.17, 0.45, 0.65, 1.8, and 2.5 at 2, 5, 10, 20, and 30 mA/cm², respectively.

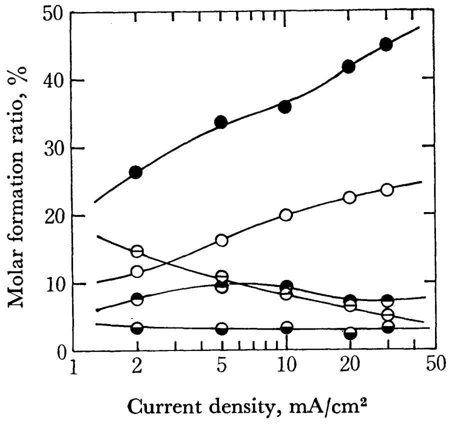

Fig. 7. Dependence of molar formation ratios of principal gaseous products on current density.
●: C_2F_6, ○: NF_3, ◓: CF_4, ⊖: CHF_3, ◒: C_2HF_5
concentration: 2.4 mol% temperature: 7±2°C

Liquid Products. Et_2N–NO fluorinated electrochemically gave a large number of liquid products together with the gaseous products descrbied above. Identification was carried out only on five principal liquid products, since the other liquid products were not obtained in sufficient amounts. Three of the principal liquid products were perfluorinated alkylation products $(C_2F_5)_2CF_3N$, $(C_2F_5)_3N$, and $(CF_3)_2C_2F_5N$. The first two were identified by their infrared spectra.⁵⁾ The last one was identified by its spectral data obtained in our laboratory.²⁾ Structural determination of the other two liquid products was unsuccessful. Nevertheless, some significant information on their structures was obtained by their infrared and ^1H NMR spectra. Their boiling points are above 70°C. Infrared spectrum of the lower boiling product (I) exibited absorption bands at 5.25 and 5.48 μ besides in the C–F stretching region, while that of the higher boiling one (II) exibited at 5.56 μ. These infrared absorptions may be assigned to the C=N stretching vibration.⁶⁾ The ^1H NMR spectra showed that both of them contained five hydrogen atoms. From the ^{19}F and ^1H NMR spectra the structure of II is supposed to be $CH_2FCH{=}NCH_2CF_3$, to which that of I would be analogous. These unsaturated compounds probably resulted from decomposition of the partially fluorinated dialkyl nitrosamines condensed in cold trap according to the following reaction;

$$\begin{matrix} R_1CHF\diagdown \\ N\text{–}NO \\ R_2\diagup \end{matrix} \xrightarrow{\text{decomposition at room temperature}} R_1CH{=}NR_2 + NOF \qquad (11)$$

Young *et al.*⁷⁾ described that although the dialkyl nitrosamines were reasonably stable thermodynamically and hydrolytically, the fluorinated compounds were unstable and lost the nitroso group readily due to increasing electronegativity of the alkyl groups. The formation of partially fluorinated dialkyl nitrosamines seemed to be apparent by appearance of a blue color presumably due to NO in liquid products condensed in cold trap.⁷⁾

Electrochemical Measurements in HF-Et_2N-NO Solutions. The anodic behavior of nickel in liquid hydrogen fluoride (HF) containing Et_2N–NO has been investigated. The electrolytic cell and experimental procedures used in this study were essentially the same as those described in the preceding paper.⁸⁾ The reference electrode was Hg/Hg_2F_2, and potentials are reported *vs.* Hg/Hg_2F_2 at

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5) C. M. Sharts, *J. Org. Chem.*, **33**, 1008 (1968).

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0°C. Galvanostatic anodic polarization data were obtained on nickel electrodes in 2.5 and 10 mol% solutions in the current density range 0.01—50.0 mA/cm^2. Tafel-like region was observed in the range of 0.1—2.0 mA/cm^2 with slopes of about 440 and 280 mV/decade at the concentrations of 2.5 and 10 mol%, respectively. These values of Tafel slope are themselves unusually high, but relatively much smaller than the values obtained for diethylamine, triethylamine,[2)] acetonitrile, and malononitrile.[9)]

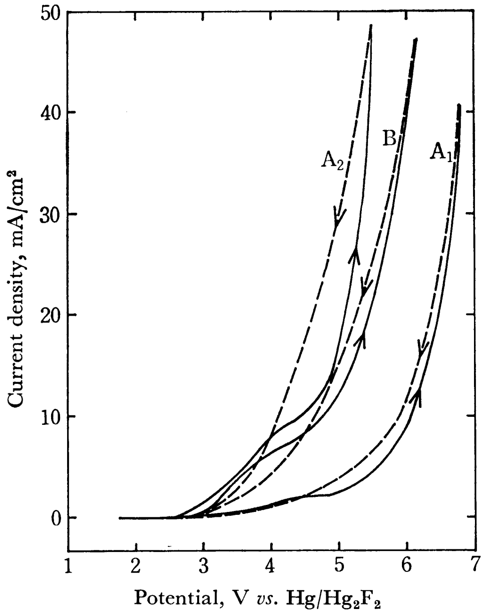

Fig. 8. Polarization curves for nickel in HF solutions of Et_2N-NO obtained by potential sweep method
A_1: new nickel in 10 mol% solution
A_2: nickel anodically polarized at 4.5V for 12 hr in 10 mol% solution
B: new nickel in 2.5 mol% solution
temperature: 0°C scan rate: 1V/min

Figure 8 shows polarization curves obtained by potential sweep method. Curves A_1 and B give the polarization curves on new nickel anodes in 10 and 2.5 mol% solutions, respectively. Compared the curve A_1 with B, it is evident that overpotential in HF solution is increased with increasing concentration of Et_2N-NO. It is also evident that nickel electrode is fairly activated when anodically biased at high potential, since an appreciable decrease in overpotential is observed on the nickel electrode anodically biased at 4.5 V for 12 hr, as shown in curve A_2 in Fig. 8. A plateau appeared around 4 V in all the curves, which is always observed for the anodic behavior of nickel in HF solution.

Figure 9 shows a polarization curve obtained by sweeping potential from 4.5 V with a scan rate of 0.2 V/sec. Cathodic current is observed below 2.4 V in curve 1, while a sharp increase in anodic current is observed above 2.6 in curve 2. The reversible fluorine potential in anhydrous hydrogen fluoride at −20°C has been reported to be +2.62 V *vs.* Hg/Hg_2F_2 by Hackerman *et al.*[10)] Assuming that the cathodic current is a reduction current of fluorine adsorbed on the nickel anode, the cathodic charge required to reduce the fluorine is estimated to be about 1.3 mcoul/cm^2. This value is close to that in HF solution containing triethylamine.[2)]

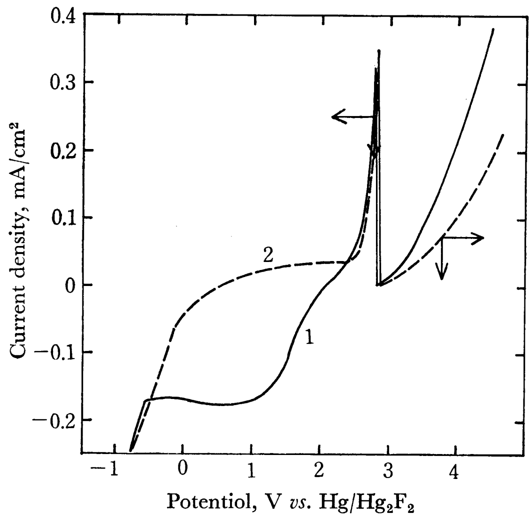

Fig. 9. Cathodic reduction curve of anodically polarized nickel electrode in 10 mol% solution.
scan rate: 0.2V/sec. temperature: 0°C

Discussion

In the present investigation on the electrochemical fluorination of Et_2N–NO, formation of the five liquid products and nine gaseous products was confirmed. However, nitrosyl fluoride which had been reasonably expected to be produced was not found in the products under any electrolysis conditions. This would be attributable to the following three reasons. Firstly, nitrosyl fluoride which is produced on the anode reacts with water contained a little in HF solution.[11)]

$$2NOF + H_2O \longrightarrow NO + NO_2 + 2HF \qquad (12)$$

Secondly, it reacts with metal, rubber, or glass within the system before reaching the cold trap.[7)] Finally, it reacts with hydrogen fluoride to form complexes.[12)]

$$NOF + nHF \longrightarrow NO^+F(HF)_n^- \qquad (13)$$

Since the anhydrous hydrogen fluoride used was dried by pre-electrolysis passing a periodic reverse current and neither NO (bp, −151.8°C) nor NO_2 (bp, 21.3°C) was detected, and since fluorination was performed at relatively low temperature, the first and second reasons would not be essential. The last one would be a chief reason for the fact that formation of NOF was not confirmed. Although NOF is formed, it remains as complex with hydrogen fluoride in HF solution and can not be detected outside the electrolytic cell.

Figure 10 shows the total current efficiencies of gaseous products in the fluorination of Et_2NH, Et_2N–NO, and Et_3N under the same operating condition. The total current efficiency of gaseous products with

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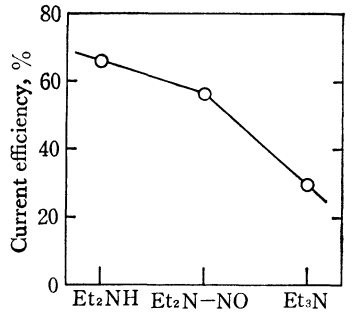


Fig. 10. Total current efficiencies of gaseous products in the fluorination of Et_2NH, Et_2N-NO, and Et_3N under the same operating conditions.
concentration: 2.2±0.2 mol%
temperature: 5±2°C
current density: 10mA/cm^2

Et_2N-NO is slightly less than that with Et_2NH, but about twice as high as that with Et_3N. Since the total current efficiency of gaseous products is dependent upon the amount of cleavage, it may be concluded that the fluorination of Et_2NH and Et_2N-NO is accompanied with violent fragmentation, on the other hand fragmentation is noticeably restrained in the fluorination of Et_3N. Relation between substrate concentration and molar ratio of fluorinated ethanes to fluorinated methanes is given in Fig. 11 for Et_2N-NO and Et_3N. The values for Et_2N-NO are higher at any concentrations, which indicates that Et_2N-NO undergoes degradation more readily by the cleavage of C–N bonds than Et_3N. As concentration becomes higher, the molar ratio for Et_2N-NO increases while that for Et_3N decreases. This is indicative that C–N bonds are cleaved more preferentially than C–C bonds with increasing concentration in the fluorination of Et_2N-NO, on the contrary less preferentially in the fluorination of Et_3N. Thus it could be attributed to the stable C–N bonds against cleavage that the fluorination of Et_3N resulted in the formation of significant amounts of liquid products having the structure of the parent molecule. Et_2NH, on the other hand, did not yield detectable amounts of liquid products, since C–N bonds were almost completely cleaved. Et_2N-NO characteristically yielded as alkylation products the three completely fluorinated tertiary amines. In addition to them, the partially fluorinated dialkyl nitrosamines free from the cleavage of N–N bonds were thought to be formed. Formation of the above liquid products in the fluorination of Et_2N-NO indicates significant effects of *N*-nitroso group on the fluorination of dialkyl amines. Difference between the fluorination reaction of Et_2N-NO and that of Et_2NH also appeared in the effect of temperature on the formation of gaseous products. The maximum value of total current efficiency of gaseous products was not found at any temperatures ranged from −40 to +30°C in the fluorination of Et_2NH, whereas it was given around 5°C for 12.7 mol% solution in the fluorination of Et_2N-NO. In view of temperature effect on the formation of gaseous products, Et_2N-NO lies between Et_2NH and Et_3N. Assuming that the temperature effect is mainly due to steric hindrance by a substituent, effect of steric hindrance is in the order $H < NO < C_2H_5$, which is consistent with experimental results.

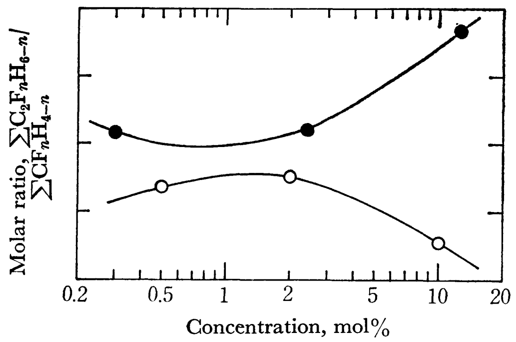
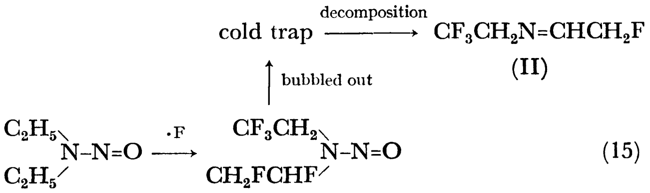


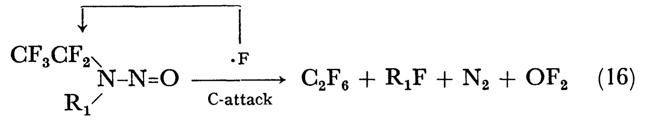
Fig. 11. Dependence of molar ratio of fluorinated ethanes to fluorinated methanes on concentration.
●: Et_2N-NO, ○: Et_3N temperature: 5±1°C
current density: 10mA/cm^2

Although the fluorination of Et_2N-NO seems to proceed simultaneously by numerous routes, a representative mechanism is postulated which accounts for the scission and alkylation observed during the fluorination. During the replacement of hydrogen by fluorine a part of partially fluorinated dialkyl nitrosamines are bubbled out of a cell;



$$\begin{array}{l} \text{cold trap} \xrightarrow{\text{decomposition}} CF_3CH_2N{=}CHCH_2F \quad \text{(II)} \\ \uparrow \text{bubbled out} \\ \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>N\text{-}N{=}O \xrightarrow{\cdot F} \begin{matrix}CF_3CH_2\\CH_2FCHF\end{matrix}\!\!>N\text{-}N{=}O \end{array} \qquad (15)$$

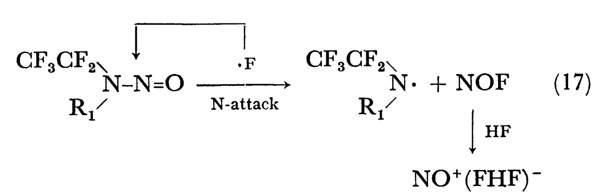
Most of the partially fluorinated dialkyl nitrosamines are followed by further fluorination since they still remain in the liquid phase because of their high solubilities in HF solution and high boiling points. During the fluorination at this stage, they are subjected to scission of bonds in molecules. Under milder operating conditions, especially at low concentration of substrate and low current density, cleavage of C–N bonds by carbon attack favorably occurs;



$$\begin{matrix}CF_3CF_2\\R_1\end{matrix}\!\!>N\text{-}N{=}O \xrightarrow[\text{C-attack}]{\cdot F} C_2F_6 + R_1F + N_2 + OF_2 \qquad (16)$$

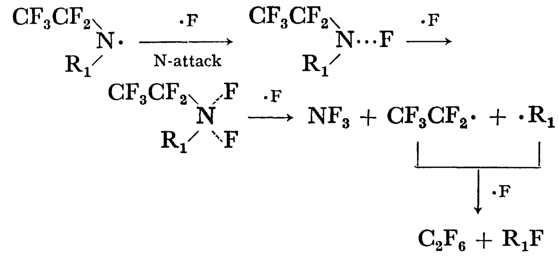
(R_1; fluorinated alkyl group)

This is evidenced by the small molar ratio of NF_3 to N_2 at low concentration and low current density. As the operating conditions become vigorous, especially at the current density of 20—30 mA/cm^2, cleavage of N–N bonds takes place more readily than that of C–N bonds;



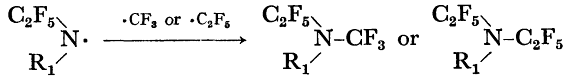
$$\begin{matrix}CF_3CF_2\\R_1\end{matrix}\!\!>N\text{-}N{=}O \xrightarrow[\text{N-attack}]{\cdot F} \begin{matrix}CF_3CF_2\\R_1\end{matrix}\!\!>N\cdot + NOF \xrightarrow{HF} NO^+(FHF)^- \qquad (17)$$

The fluorinated dialkyl amine radicals are successively attacked by fluorine until NF_3 is formed;



(18)

Fluorinated primary and secondary amines were completely absent in the products obtained in the fluorination of Et_2N–NO, which had been claimed as one of the characteristic features in electrochemical fluorination of nitrogen-containing compounds.[13] Nitrogen in an amine molecule is specifically oriented to Ni electrode, so that it is preferentially attacked by fluorine. NF_3 is formed probably through the transient state of fluorinated secondary and primary amines which are adsorbed on the nickel anode, as described in equation 18. This process would be explained well if fluorination took place between a loose complex of NiF_2 and ·F or F_2 and the substrate adsorbed on the anodic film.[14] The perfluoro dialkyl amine radicals are alkylated at nitrogen with perfluoro carbon radicals to produce perfluoro tertiary amines;



(19)

(R_1; C_2F_5 or CF_3)

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[13] J. A. Young and R. D. Dresdner, *J. Amer. Chem. Soc.*, **80**, 1889 (1958).

[14] L. G. Spears and N. Hackerman, *J. Electrochem. Soc.*, **115** 452 (1968).