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The Electrochemical Fluorination of *s*-Triazines

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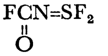
A great many papers have described the fluorination of nitrogen compounds with a carbon - nitrogen multiple bond.[1] However, the information given in the literature about the electrochemical fluorination of nitrogen compounds has not extended to nitriles and imines other than acetonitrile[2] and guanidine.[3] The present investigation was undertaken mainly in order to study the general behavior of the carbon - nitrogen multiple bond upon electrochemical fluorination.[*1] Trifluoroacetonitrile and perfluoroalkyl iminosulfur difluorides were subjected to electrochemical fluorination. Furthermore, such *s*-triazines as cyanuric fluoride, thiocyanuric acid and 1,3,5-triamino-*s*-triazine were also fluorinated.

It was found that, upon electrochemical fluorination, these samples were cleaved extensively, giving fluorocarbons, nitrogen trifluoride, and perfluoroamines. The evolution of nitrogen gas was also observed. In addition, sulfur hexafluoride was obtained from the compounds containing sulfur.

When trifluoroacetonitrile (bp 65°C) was subjected to fluorination electrochemically (reaction conditions: sample feed rate, 14 m*l*/min, He, 20 m*l*/min; anodic current density, 2.0 A/dm^2; cell voltage, 5.7—6.7 V; cell temp, 13°C; NaF added, 5 g), the product consisted of tetrafluoromethane (28 mol%), trifluoromethane (2%), hexafluoroethane (28%), and nitrogen trifluoride (42%). When the sample feed rate was increased (27.1 m*l*/min), pentafluoroethyldifluoroamine was obtained in a very low yield ($<1\%$), along with other fluorinated compounds. The product composition (mol%) was as follows: tetrafluoromethane (21%), trifluoromethane (1%), hexafluoroethane (33%), nitrogen trifluoride (44%) and pentafluoroethyldifluoroamine (1%). Similarly, trifluoromethyl iminosulfur difluoride (bp −7—−5°C), pentafluoroethyl iminosulfur difluoride (bp 22—24°C), and *N*-fluoroformyl iminosulfur difluoride (bp 54°C) underwent breakdown upon electrochemical fluorination, giving the compounds depicted below:

Sample		Products[*2]
$CF_3N{=}SF_2$	→	CF_4, NF_3, SF_6, CF_3NF_2, $(CF_3)_2NF$ and CHF_3
$C_2F_5N{=}SF_2$	→	C_2F_6, SF_6, NF_3, CF_4, $C_2F_5NF_2$, C_2F_5H and CHF_3
 $F\underset{\underset{O}{\|}}{C}N{=}SF_2$	→	COF_2, NF_3, SF_6, CF_4 and CF_3OF

The reaction conditions and the results with the electrochemical fluorination of *s*-triazines as well as methyl thiocyanate and methyl isothiocyanate are shown in Table 1. In this fluorination, only cleaved products were yielded; tetrafluoromethane and nitrogen trifluoride were the main products from these starting materials. The results are in contrast to those obtained by the fluorination of these compounds with elementary fluorine. It has been reported by Ruff that the fluorination of trifluoroacetonitrile[4] and perfluoroalkyl iminosulfur difluoride[5] with fluorine gave fully-fluorinated,

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[1] G. E. Coates, J. Harris and T. Sutcliffe, *J. Chem. Soc.*, **1951**, 2762; J. A. Cuculo and L. A. Bigelow, *J. Amer. Chem. Soc.*, **74**, 710 (1952); P. Robson, V. C. R. McLoughlin, J. B. Hynes and L. A. Bigelow, *ibid.*, **83**, 5010 (1961); H. J. Emeléus and G. L. Hurst, *J. Chem. Soc.*, **1962**, 3276; B. C. Bishop, J. B. Hynes and L. A. Bigelow, *J. Amer. Chem. Soc.*, **84**, 3409 (1962); R. D. Dresdner, J. Merritt and J. P. Royal, *Inorg. Chem.*, **4**, 1228 (1965).

[2] J. H. Simons, U. S. 2519983 (1950).

[3] A. Engelbrecht and E. Nachbaur, *Monatsh. Chem.*, **90**, 371 (1955).

[*1] The electrochemical fluorination of hydrogen cyanide and cyanogen will be described elsewhere.

[*2] The products are shown in the order of the amounts formed.

[4] J. K. Ruff, *J. Org. Chem.*, **32**, 1675 (1967).

[5] M. Lustig and J. K. Ruff, *Inorg. Chem.*, **4**, 1444 (1965).

Table 1. Reaction conditions and the results with the fluorination of *s*-triazines

Run No.	Sample	Sample fed (mol)	Electricity passed[*a] (A. hr)	Fluorocarbons obtained (g)	Molar ratio[*b]	Product composition (mol %)							
						CF_4	CHF_3	NF_3	CF_3NF_2	$(CF_3)_2NF$	$CF_2(NF_2)_2$	SF_6	CF_3SF_5
1	$(CNF)_3$	0.148	79	56.3	4.64	48		47	5	+			
2	$(CNSH)_3$	0.150	122	41.4	2.39	24		30	7	6		33	
3	$(CNNH_2)_3$	0.150	176	52.4	3.26	26		64	5	4	1		
4	CH_3SCN	0.150	90	26.8	1.81	34	11	39	1			3	12
5	CH_3NCS	0.150	113	32.7	2.67	42	30	25	+			3	+

[*a] Electrolysis was continued until the cell voltage was raised up to 7.6 V.

[*b] (total mol of products/mol of sample)

saturated compounds as the main products, without any fission of the carbon - nitrogen bond or the nitrogen - sulfur bond. However, upon electrochemical fluorination, no formation of any fluorinated compounds, such as R_fNFSF_5 (R_f = trifluoromethyl, pentafluoroethyl and fluoroformyl) and *N,N*-difluoroaminosulfur pentafluoride, was detected from the corresponding starting material, even when an increased amount of sample was fed into anhydrous hydrogen fluoride; a higher feed rate of the sample makes the reaction milder.[6] Further perfluoroalkylazo compounds (*e. g.*, $CF_3N{=}NCF_3$ and $C_2F_5N{=}NC_2F_5$) which have been reported to be found in the products of the direct fluorination of these compounds with an unsaturated carbon - nitrogen bond[7] were not detected in the present fluorination reaction.

Experimental

Materials. Trifluoroacetonitrile,[8] trifluoromethyl iminosulfur difluoride, pentafluoroethyl iminosulfur difluoride,[9] *N*-fluoroformyl iminosulfur difluoride,[10] cyanuric fluoride[11] and thiocyanuric acid[12] were prepared and purified by the method in the literature. The 1,3,5-triamino-*s*-triazine, methyl thiocyanate, and methyl isothiocyanate were obtained commercially.

The purity of the anhydrous hydrogen fluoride was better than 99%.

Apparatus and Procedures. Two types of electrolytic cells were employed in these experiments. For the fluorination of trifluoroacetonitrile, trifluoromethyl iminosulfur difluoride, pentafluoroethyl iminosulfur difluoride, and *N*-fluoroformyl iminosulfur difluoride, an iron cell (300 m*l* capacity) was employed. A monel cell (1 *l* capacity) was employed for the others. The anodic surface areas were 7.7 dm² and 9.2 dm² respectively. The bottoms of these cells were equipped with a bubbler. In both cases, the anodic current density was 2.0 A/dm².

As for the gaseous samples, the procedures are essentially the same as those described in the preceding paper,[13] but the reflux condenser was kept at −20°C and the gaseous product was analysed by studying the G.C. (column; FC 43[*3] 66% on Celite 545 SK, KelF #3[*3] 30% on Chromosorb PAW) and IR spectra, taking the sample directly from the sampling valve fixed next to the hydrogen fluoride absorber.

For the other samples the electrolysis were carried out by batch. The procedures thereafter were the same as have been described previously.[6] The tetrafluoromethane and nitrogen trifluoride were analysed by G.C. (conditions: column, silica gel 60—80 mesh, 1.5 m length×3 mm id; carrier gas, He; temp., 0°C).

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[6] S. Nagase, T. Abe and H. Baba, This Bulletin, **40**, 684 (1967).

[7] J. B. Hynes and L. A. Bigelow, *J. Amer. Chem. Soc.*, **84**, 2751 (1962); J. A. Attaway, R. H. Groth and L. A. Bigelow, *ibid.*, **81**, 3599 (1959).

[8] H. Gilman and R. G. Jones, *ibid.*, **65**, 1458 (1943).

[9] W. C. Smith, C. W. Tullock, R. D. Smith and V. A. Engelhardt, *ibid.*, **82**, 551 (1960).

[10] U. Biermann and O. Glemser, *Chem. Ber.*, **100**, 3795 (1967).

[11] A. F. Maxwell, J. S. fry and L. A. Bigelow, *J. Amer. Chem. Soc.*, **80**, 548 (1958).

[12] A. W. Hofmann, *Ber.*, **18**, 2201 (1885).

[13] S. Nagase, T. Abe and H. Baba, This Bulletin, **42**, 2062 (1969).

[*3] Minnesota Mining and Manufacturing Co., Ltd.