The Fluorination of Gaseous Haloethylenes[*1]

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An earlier paper of this series described the electrochemical fluorination of ethylene, which was shown to be fluorinated without any significant polymerization or fragmentation.1) The present paper will give the results of the work extended to the electrochemical fluorination of gaseous halogenated ethylenes, including fluoroethylene, chloroethylene, 1, 1-difluoroethylene, chlorotrifluoroethylene, and tetrafluoroethylene.

So far, there has been no detailed report on the electrochemical fluorination of gaseous haloolefins.[*2] Under controlled conditions, these gases were found to be fluorinated smoothly, giving various kinds of saturated fluorinated products in a reasonable total yield. The general features of the reaction can be explained upon the assumption that the fluorination proceeds by a free-radical mechanism.1)

The reaction conditions for each sample are shown in Table 1, while the results obtained are presented in Tables 2, 3, 4, 5 and 6. The effects of the operating conditions on the product distribution were shown distinctly in the fluorination of fluoroethylene; the smaller feed rate and the lower temperature resulted in a more vigorous reaction, giving a larger amount of hexa- and pentafluorinated ethanes, whereas the increased amount of sodium fluoride made the reaction milder, as was the case in the fluorination of methane.2) Since a very similar tendency was observed in the fluorination of 1, 1-difluoroethylene, only two typical runs are shown in the tables. The feed rate affected all the samples examined here similarly as had also been observed in the fluorination of ethylene and ethane.1)

No simple conclusion regarding the effect of other reaction conditions on the fluorination of chloroethylene and chlorotrifluoroethylene can be drawn, since our experiments gave very complicated results, with a wide variety of products, including chlorinated ones.

TABLE 1. CONDITIONS FOR THE FLUORINATION

Run[a)] No.	Sample[b)] feed rate ml/min	Total amount of sample fed mol	Electricity passed A. hr	NaF used g	Temp. °C
		Fluoroethylene			
1	29	0.281	70	10	5—6
2	51	0.285	41	10	5—6
3	75	0.282	28	10	5—6
4	53	0.228	32	50	5—6
5	53	0.242	35	10	−10[c)]
6	53	0.278	39	10	16—17
		Chloroethylene			
1	20	0.208	79	10	5—6
2	52	0.301	43	10	5—6
3	72	0.293	31	10	5—6
4	54	0.300	41	50	5—6
5	53	0.302	42	10	−10[c)]
6	54	0.441	60	10	16
		1, 1-Difluoroethylene			
1	53	0.297	42	10	5—6
2	52	0.299	43	50	5—6
		Chlorotrifluoroethylene			
1	25	0.237	68	10	5—6
2	51	0.198	28	10	5—6
3	61	0.239	29	10	5—6
4	51	0.236	34	50	5—6
5	55	0.238	33	10	−10—−9[c)]
6	51	0.236	34	10	15—16
		Tetrafluoroethylene			
1	20	0.217	82	10	5—6
2	44	0.225	36	10	5—6

a) All the experiments were carried out with the anodic current density of 2.2 A/dm^2.
b) Gas volume is expressed at normal condition.
c) The cell temperature was raised to 6°C at the end of the reaction.

The notable products from fluoroethylene were 1, 1 - difluoroethane and 1, 1, 1 - trifluoroethane. The mechanistic scheme proposed earlier for the formation of these fluoroethanes from ethylene1) could also apply in the present case; the addition of hydrogen fluoride to the double bond of fluoroethylene would yield the former, followed by the replacement of hydrogen by fluorine to yield the latter in this case.

[*1] "Electrochemical Fluorination of Gases," Part IV. Presented in part at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966.

1) S. Nagase, K. Tanaka, H. Baba and T. Abe, This Bulletin, **39**, 219 (1966).

[*2] Chloroethylene, and chlorotrifluoroethylene and tetrafluoroethylene have been listed among halogenohydrocarbons in patents [Ref. 5 and Farbenfabriken Bayer A.-G., Brit. Pat., 740723 (1955)] but no details are given for these gaseous haloethylenes.

2) S. Nagase, K. Tanaka and H. Baba, *ibid.*, **38**, 834 (1965).

TABLE 2. RESULTS IN THE FLUORINATION OF FLUOROETHYLENE

Run No.	Total[a] yield %	Total[b] current eff. %	Product[c] composition, mol%[c,d]								
			CF_3CF_3	CHF_2CF_3	CH_2FCF_3	CHF_2CHF_2	CH_3CF_3	CH_3CHF_2	CF_4	CHF_3	n-C_4F_{10}
1	78.9	52.8	43.9	18.5	20.0	2.8	7.3	—	1.7	3.9	1.9
2	66.5	62.3	16.5	29.7	14.2	15.8	14.9	4.5	1.6	2.5	0.3
3	52.5	59.5	13.2	15.7	10.0	11.8	33.6	9.9	1.5	4.3	—
4	51.3	46.2	19.1	15.7	13.3	24.6	9.2	7.0	1.5	9.3	0.3
5	42.0	45.0	36.3	28.6	5.6	8.0	5.6	5.5	0.7	9.2	0.5
6	60.2	58.7	25.0	13.5	13.4	15.1	13.6	9.3	1.2	2.4	1.5

a) Yields (mol%) in this and in the following tables were calculated on the basis of the amount of the sample fed.

b) The calculation of the current efficiency was made under the similar assumption as before.[1] A few examples of the assumed equations for the fluorination of fluoroethylene were as follows.

$C_2H_3F+8F \rightarrow CF_3CF_3+3HF$ (1) $C_2H_3F+H+F \rightarrow CH_3CHF_2$ (2) $C_2H_3F+10F \rightarrow 2CF_4+3HF$ (3)

Total current efficiency shown is the sum total of the current efficiency for each component. The current efficiency was calculated in a similar manner for the fluorination of 1,1-difluoroethylene and tetrafluoroethylene.

c) Except n-C_4F_{10}, these were identical compounds with those obtained in the fluorination of ethylene. (The amount of CHF_3 formed was negligibly small in the case of the ethylene.)[1]

d) A small amount of unidentified product (<0.5 g) was found in the rectification residue of the fluorinated products from fluoroethylene and other samples.

TABLE 3. RESULTS IN THE FLUORINATION OF CHLOROETHYLENE

Run No.	Total yield %	Total[a] current eff. %	Product composition, mol%						
			CF_3CF_3	CHF_2CF_3	$CClF_2CF_3$[b]	CH_2FCF_3	CHF_2CHF_2	CHF_2CClF_2[b]	CH_2FCClF_2[e]
1	65.9	36.4	39.4	6.9	14.2	2.6	1.1	7.7	4.2
2	48.7	59.2	9.6	5.4	18.0	5.5	—	22.6	14.2
3	18.9	31.1	9.7	10.7	15.2	5.6	1.0	15.0	11.5
4	30.0	35.7	11.4	1.8	18.9	1.3	—	17.2	28.9
5	35.3	46.3	8.0	11.5	12.4	8.8	4.1	25.2	6.0
6	65.7	75.4	5.5	4.6	9.2	5.9	4.6	24.4	26.7

Run No.	Product composition, mol%									
	CH_3CF_3	CF_4	CHF_3	$CClF_3$[c]	$CHClF_2$[c]	CCl_2F_2[c]	$CClF_2CClF_2$[b]	$CHClFCClF_2$[d]	CCl_2FCClF_2[b]	n-C_4F_{10}[b]
1	0.6	7.1	1.0	7.5	0.7	—	4.6	0.9	0.9	0.6
2	3.1	0.7	4.2	2.0	1.4	0.8	12.5	—	—	—
3	4.9	1.1	8.3	3.1	3.4	—	10.5	—	—	—
4	2.6	3.1	2.3	2.1	2.5	—	3.3	3.8	0.8	—
5	5.7	0.9	4.9	1.6	0.8	0.9	9.2	—	—	—
6	1.9	1.0	2.7	1.2	0.8	1.3	8.2	2.0	—	—

a) A few examples of the assumed equations for calculation of the current efficiency:

$C_2H_3Cl + 10F \rightarrow CF_3CF_3 + ClF + 3HF$ (1) $C_2H_3Cl + Cl + 7F \rightarrow CClF_2CClF_2 + 3HF$ (3)

$C_2H_3Cl + 8F \rightarrow CF_3CClF_2 + 3HF$ (2) $C_2H_3Cl + H + 5F \rightarrow CH_3CF_3 + ClF + HF$ (4)

Current efficiency was calculated in a similar manner for the fluorination of chlorotrifluoroethylene.

b), c), d), e) Infrared spectra of these compounds, agree with those listed in the following references respectively: "Infrared Spectral Data," American Petroleum Institute, Research Project 44, Carnegie Institute Technology, 1959, Serial number, 1312, 1338, 1038, 1036 and 1370, E. K. Plyer and W. S. Benedict, *J. Research Natl. Bur. Standards*, **47**, 202 (1951); J. D. Park, W. R. Lycan and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 711 (1951); and that of an authentic specimen.

The rather large amount of 1,1,1-trifluoroethane formed from 1,1-difluoroethylene indicates the very easy addition of hydrogen fluoride to 1,1-difluorovinyl compounds;[3] the other products were mainly formed by the progressive fluorination of the trifluoroethane.

Chlorination reaction took place to some extent

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[3] A. L. Henne and J. B. Hinkamp, *J. Am. Chem. Soc.*, **67**, 1197 (1945).

TABLE 4. RESULTS IN THE FLUORINATION OF 1, 1-DIFLUOROETHYLENE

Run No.	Total yield %	Total current eff. %	Product composition, mol%						
			CF_3CF_3	CHF_2CF_3	CH_2FCF_3	CH_3CF_3	CF_4	CHF_3	n-C_4F_{10}
1	66.3	33.9	23.4	4.8	15.3	46.9	8.9	0.3	0.4
2	65.0	23.3	7.4	6.7	20.0	61.3	3.5	0.9	0.2

TABLE 5. RESULTS IN THE FLUORINATION OF CHLOROTRIFLUOROETHYLENE

Run No.	Total yield %	Total current eff. %	Product composition, mol%								
			CF_3CF_3	$CClF_2CF_3$	CF_4	CHF_3	$CClF_3$	CCl_2F_2	$CClF_2CClF_2$	CHF_2CClF_2	n-C_4F_{10}
1	71.0	17.7	22.0	31.9	18.6	2.8	5.9	—	16.7	—	2.1
2	69.5	29.6	15.3	41.1	17.2	1.4	6.6	3.6	13.6	0.8	0.4
3	70.2	32.0	8.0	53.3	8.9	0.5	9.8	3.8	13.4	1.6	0.7
4	59.1	20.0	1.5	57.6	9.2	0.5	18.1	2.2	9.5	1.3	0.1
5	48.9	21.1	8.4	51.7	19.2	0.6	5.1	3.5	10.6	0.6	0.3
6	67.6	25.8	6.5	66.3	4.1	0.2	6.0	1.6	13.4	0.8	1.1

TABLE 6. RESULTS IN THE FLUORINATION OF TETRAFLUOROETHYLENE

Run No.	Total yield %	Total current eff. %	Product composition, mol%				
			CF_3CF_3	CHF_2CF_3	CF_4	CHF_3	n-C_4F_{10}
1	86.1	12.2	73.5	2.2	20.4	0.4	3.5
2	80.1	26.9	62.2	4.5	29.8	1.3	2.2

during fluorination in chloroethylene, which gave various products, including di- and trichlorides. Dichlorinated products were obtained even in the fluorination of chlorotrifluoroethylene. Such chlorination has been reported in the electrochemical fluorination of a gaseous halomethane[4] and of liquid chlorohydrocarbons.[5] The chlorination might be due either to the formation of chlorine fluoride, known to be a powerful chlorinating agent, or to the liberation of free chlorine.

The interesting products from chlorotrifluoroethylene and tetrafluoroethylene were small amounts of hydrogen-containing compounds. This hydrogen may have been derived *via* the addition of hydrogen fluoride to the double bond. Under the present reaction conditions, such addition may have occurred to some extent even in these highly halogenated ethylenes.

A small amount of a tarry polymeric material was found in the electrolytic cell after the fluorination of each sample.

Experimental

Materials. Fluoroethylene (99.9%), chloroethylene (99.9% min), and 1, 1-difluoroethylene (99.0% min) were purchased from the Matheson Co. Chlorotrifluoroethylene was prepared by the dechlorination of 1, 1, 2-trichlorotrifluoroethane with zinc dust in ethanol.[6] Tetrafluoroethylene was synthesized by the pyrolysis of chlorodifluoromethane.[7] The purity of these two olefins, rectified so as to be better than 99.8%, was confirmed through gas chromatographic analysis. Hydrogen fluoride rated as better than 99% pure was furnished by the Daikin Industries Co.; it was used as has frequently been described.

Apparatus and Procedure. The electrochemical fluorination apparatus used was the same as that described in a preceding paper.[4] The fluorination procedure, which has previously been described in detail,[1] was essentially as follows: a known amount of the sample gas was introduced continuously into 1 *l* of hydrogen fluoride, containing sodium fluoride dissolved as a conductivity additive, while the current was conducted through; the products were freed from hydrogen fluoride and oxygen difluoride, and condensed. For the identification and the analysis of the products, low-temperature rectification, with molecular weight measurements, and then gas chromatography (column: silica gel, carrier: helium) and infrared spectrum mesurements were used, as has been described previously.[1]

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[4] S. Nagase, H. Baba and T. Abe, This Bulletin, **39**, 2304 (1966).

[5] British Thomson-Houston Co., Ltd., Brit. Pat., 668609 (1952).

[6] E. G. Locke, W. R. Brode and A. L. Henne, *J. Am. Chem. Soc.*, **56**, 1726 (1934).

[7] J. D. Park, A. F. Benning, F. B. Downing, J. F. Laucius and R. C. McHarness, *Ind. Eng. Chem.*, **39**, 354 (1947).