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The Chlorofluorination of Ethylene, Ethane, Fluoroethylene and Methane*[1]

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This novel electrochemical chlorofluorination involves the passage of each of the title materials, together with chlorine, through liquid hydrogen fluoride containing sodium fluoride. Chlorofluoroethanes were produced directly from ethylene, ethane, and fluoroethylene, while chlorofluoromethanes were produced directly from methane. Carbon tetrachloride, chloroform, and phosgene could also be used as a source of chlorine for the chlorofluorination reaction. Thionyl and sulfuryl chlorides, and sulfur mono- and di-chlorides did not act as chlorinating reagents.

The previous papers in this series[1,2] have shown that when monochlorohydrocarbons were subjected to the electrochemical fluorination, di- and tri-chlorinated fluorocarbons were produced as by-products. A similar result has been described in connection with the electrochemical fluorination of methylene chloride.[3]

The present work is an extension of these findings and deals with the electrochemical chlorofluorination of ethylene, ethane, fluoroethylene, and methane. It was found that when a gaseous mixture of chlorine and a hydrocarbon was introduced into liquid hydrogen fluoride containing a conductivity additive (sodium fluoride), while a current was being passed through it, the chlorofluorination as well as the fluorination of the hydrocarbon took place.

The common methods for the preparation of chlorofluorinated hydrocarbons involve the replacement of chlorine atoms with fluorine by using organic chloro compounds as the starting materials.[4] An exceptional case, however, is found in the reaction of ethylene with chlorine trifluoride; here chlorofluorinated ethanes are produced directly from ethylene.[5]

Although the electrochemical fluorination[6,7] and chlorination[8] have been known, the significance of the electrochemical process described herein is that fluorination and chlorination take place simultaneously, and the chlorofluoro compounds can be produced directly from hydrocarbons. Organic chlorine-containing compounds, such as carbon tetrachloride, chloroform, and phosgene, also serve as sources of chlorine in the present chlorofluorination reaction.

Results and Discussion

The reaction conditions for the chlorofluorination of ethylene, ethane, fluoroethylene, and methane by the use of a chlorine-hydrogen fluoride system are shown in Table 1. The results obtained with ethylene, ethane, and fluoroethylene are presented in Table 2, and those obtained with methane, in Table 3.

Ethylene, ethane, and fluoroethylene yielded chlorofluoroethanes, such as chloropentafluoroethane, 1-chloro-1, 1, 2, 2-tetrafluoroethane, 1, 2-dichlorotetrafluoroethane, 1-chloro-1,1, 2-trifluoroethane, and 1-chloro-1, 1-difluoroethane, as well as non-chlorinated fluoroethanes in a reasonable total yield. Similarly, methane afforded chlorofluoromethanes, such as chlorotrifluoromethane, chlorodifluoromethane, dichlorodifluoromethane, dichlorofluoromethane, and chlorofluoromethane, together with fluoromethanes.

The halogenation reaction was effected without any such difficulty as the blocking of the current or an explosion. Although various kinds of chlorofluorinated compounds were produced, the total yield of those products reached as high as 50%

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

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

[2] S. Nagase, T. Abe and H. Baba, *ibid.*, **40**, 684 (1967).

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

[4] A. M. Lovelace, D. A. Rausch and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Co., New York, (1958), p. 31.

[5] G. Schiemann and B. Cornils, *Chem. Ber.*, **98**, 3418 (1965).

[6] J. H. Simons, U. S. Pat. 2519983 (1950); Japanese Pat. 224948 (1956); J. H. Simons *et al.*, *J. Electrochem. Soc.*, **95**, 47 (1949).

[7] See, for example, S. Nagase, *Fluorine Chemistry Reviews*, Vol. 1 (1967), Marcel Dekker, Inc., New York, in press.

[8] F. N. Ruehlen, G. B. Wills and H. M. Fox, *J. Electrochem. Soc.*, **111**, 1107 (1964).

TABLE 1. CONDITIONS FOR THE CHLOROFLUORINATION (Chlorine - hydrogen fluoride system)

Anodic current density, 1.7 A/dm^2;
cell voltage, 6.5—7.5 V; cell temperature, 10—12°C;
NaF, 5 g; He, 25 m*l*/min

Run No.	Sample* feed rate m*l*/min	Total amount of sample fed mol	Chlorine* feed rate m*l*/min	Electricity passed A·hr
		Ethylene		
1	20	0.107	10	26
2	20	0.107	20	27
		Ethane		
3	20	0.107	10	27
4	20	0.107	20	27
		Fluoroethylene		
5	14	0.083	10	30
6	19	0.109	20	28
		Methane		
7	20	0.107	10	26
8	20	0.054	30	13

* Gas volume is expressed in normal condition.

in the case of ethane. The yield, however, was low in the case of methane, which gave a chlorinated product besides chlorofluorinated and fluorinated products.

Most of the chlorinated fluoro compounds were mono-chlorinated, but di- and tri-chlorinated compounds were also produced. It may be possible that the chlorine in the chlorofluorinated compounds primarily formed was replaced by fluorine in the course of the reaction. The non-chlorinated fluoro compounds obtained were principally similar to those formed by the electrochemical fluorination of each of these samples in the absence of chlorine.[9,10]

The higher ratio of the feed rate of chlorine to that of the sample did not always increase the yield of chlorofluorinated compounds. This may be partly due to the insolubility of chlorine in hydrogen fluoride[11] and to the combination of the two chlorine radicals formed instead of their incorporation into the halogenated products.

The results of chlorofluorination by the use of chlorohydrocarbon - hydrogen fluoride systems are shown in Table 4.[*2] The main products were the same as those obtained in the chlorine-hydrogen fluoride system. With carbon tetrachloride as a source of chlorine, ethylene afforded chlorofluorinated compounds in the highest yield (45.7%).

Phosgene also served as the source of chlorine in this chlorofluorination reaction. For example, when ethylene, together with phosgene, was introduced into hydrogen fluoride and subjected to electrochemical halogenation (reaction conditions: ethylene, 20 m*l*/min; total amount of ethylene, 0.107 mol; phosgene, 19 m*l*/min; helium, 25 m*l*/min; sodium fluoride, 5 g; anodic current density, 1.7 A/dm^2; electricity passed, 26 A·hr; cell voltage, 6.6 V; cell temperature, 11°C), a product with the following composition was obtained in a total yield of 95.6%, in a 19.4% yield of chlorofluorinated compounds, and in a total current efficiency of 62.7%: hexafluoroethane (14.1%), pentafluoroethane (9.2%), chloropentafluoroethane (2.6%), 1, 1, 1, 2-tetrafluoroethane (7.7%), 1, 1, 2, 2-tetrafluoroethane (10.1%), 1-chloro-1, 1, 2, 2-tetrafluoroethane (5.5%), 1, 1, 1-trifluoroethane (22.8%), 1-chloro-1, 1, 2-trifluoroethane (6.3%), 1, 1-difluoroethane (10.1%), 1-chloro-1, 1-difluoroethane (5.1 %), carbon tetrafluoride (1.3%), fluoroform (3.5 %), chlorotrifluoromethane (0.7%), and methylene fluoride (1.0%). Phosgene was also fluorinated, and so some of the carbon tetrafluoride and chlorotrifluoromethane must have been derived from phosgene.

When ethane was used in place of ethylene, chlorofluorinated as well as fluorinated products were obtained in a total yield of 63.6% and in a total current efficiency of 69.0%. The yield of chlorofluorinated compounds, however, was only 1.2%. A considerable amount of ethyl chloride was found. The product consisted of hexafluoroethane (1.8%), pentafluoroethane (4.7%), 1, 1, 1, 2-tetrafluoroethane (5.0%), 1, 1, 2, 2-tetrafluoroethane (8.5%), 1, 1, 1-trifluoroethane (31.6%), 1-chloro-1, 1, 2-trifluoroethane (0.6%), 1, 1-difluoroethane (15.9%), 1-chloro-1, 1-difluoroethane (1.3 %), carbon tetrafluoride (1.2%), fluoroform (2.7 %), methylene fluoride (0.6%), and ethyl chloride (26.1%).

Interestingly, the electrochemical chlorofluorination did not take place when such inorganic chlorine-containing compounds as thionyl chloride, sulfuryl chloride, and sulfur mono- and di-chlorides were used. Some of these are often used as chlorinating agents in conventional chemical reactions. In the present reaction, the inorganic compounds were fluorinated preferentially to yield fluorinated sulfur compounds, such as sulfur hexafluoride and sulfuryl fluoride; most of the starting hydrocarbons were recovered unchanged, together with a small amount of fluorinated products. Only in the case of sulfur monochloride, a trace of dichlorodifluoromethane was formed from ethane.

The mechanism for electrochemical fluorination is not completely understood as yet,[7] but the

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9) S. Nagase, K. Tanaka and H. Baba, This Bulletin, **38**, 834 (1965).

10) S. Nagase, K. Tanaka, H. Baba and T. Abe, *ibid.*, **39**, 219 (1966).

11) L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents," Wiley, New York. (1953), p. 192.

[*2] In this reaction, carbon tetrachloride or chloroform was also fluorinated to give mono-, di-, tri-, and tetra-fluorinated methanes, as has already been shown by their electrochemical fluorination. [Ref. 8; H. Kisaki, S. Mabuchi and T. Sakomura, *Denki Kagaku (J. Electrochem. Soc. Japan)*, **34**, 29 (1966)].

TABLE 2. RESULTS WITH ETHYLENE,

Run No.	Total* yield %	Cl-F** compound yield %	Total*** current efficiency %	CF_3CF_3	CHF_2CF_3	$CClF_2CF_3$	CH_2FCF_3	CHF_2CHF_2	Product CHF_2CClF_2
1	64.9	17.6	45.8	20.3	6.5	2.7	5.8	9.2	5.8
2	62.1	5.5	45.3	26.1	10.1	2.4	7.7	4.8	2.1
3	79.8	31.8	68.8	15.8	4.7	3.7	8.4	9.3	10.9
4	89.7	49.5	67.8	5.2	2.8	1.5	6.7	5.7	4.3
5	68.6	27.0	30.4	31.4	3.7	11.3	8.3	11.5	20.5
6	33.8	22.8	18.4	6.0	6.0	20.1	9.2	7.3	28.3

* In the calculation, the total number of mole of the products including fragmented ones was divided

** Total yield of chlorofluorinated products.

*** Examples of the assumed equation for the calculation of the current efficiency:

$$CH_3CH_3 + 12F = CF_3CF_3 + 6HF \text{ (12 Farady)}$$

Total current efficiency is the total sum of the current efficiency for each component. The current

TABLE 3. RESULTS

Run No.	Total yield %	Cl-F compound yield %	Total current efficiency %	CF_4	CHF_3	$CClF_3$	CH_2F_2	Product $CHClF_2$
7	30.0	6.1	13.5	12.5	11.2	6.2	21.6	3.7
8	24.2	11.7	12.4	10.8	7.7	10.0	19.2	13.9

TABLE 4. THE CHLOROFLUORINATION OF

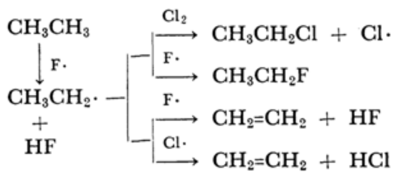
(Chlorohydrocarbon - hydrogen

Reaction conditions: sample feed rate, 20 m*l*/min; total amount of sample fed, 0.107 mol; A/dm^2; electricity passed, 39 A·hr; cell voltage, 5.5—6.0 V; cell temperature, 5°C (run 9),

Run No.	Sample	Source of chlorine	Total* yield %	Cl-F compound yield %	Total current efficiency %	CF_3CF_3	CHF_2CF_3	$CClF_2CF_3$	Product CH_2FCF_3
9	$CH_2=CH_2$	CCl_4	47.0	10.4	20.6	6.0	8.7	6.4	19.4
10	$CH_2=CH_2$	CCl_4	100.3	45.7	47.2	9.0	7.9	5.9	7.8
11	CH_3CH_3	CCl_4	88.2	29.2	48.9	14.3	3.2	1.2	10.2
12	$CH_2=CHF$	CCl_4	63.9	41.7	22.8	5.9	0	17.8	9.1
13	CH_3CH_3	$CHCl_3$	36.7	4.1	16.2	17.9	0	0	6.7

*1 The products with one carbon atom expected to be derived from carbon tetrachloride in runs 9, 10, efficiency and product composition.

general feature of the present electrochemical reaction appears to be a free-radical one. For example, in the case of ethane in the chlorine-hydrogen fluoride system, the initial steps of the reaction may be considered to be as follows:



Under the conditions of a high concentration of fluorine radical and its strong reactivity, these compounds would be further fluorinated to yield polyfluorinated compounds by the radical reaction. Similarly, if chlorohydrocarbons are the source of chlorine, chlorine liberated by fluorine from them would take part in the radical reaction. In the carbon tetrachloride - hydrogen fluoride system, the presence of hexachloroethane in the product may suggest the formation of a trichloromethyl radical from carbon tetrachloride.

ETHANE AND FLUOROETHYLENE

composition, %								
$CClF_2CClF_2$	CH_3CF_3	CH_2FCClF_2	CH_3CClF_2	CF_4	CHF_3	$CClF_3$	CH_2F_2	Others, %
0.7	23.6	5.0	7.9	0.7	2.0	3.5	1.2	CH_3CHF_2 (3.7) $CHClF_2$ (1.4)
0	37.7	0	1.5	1.5	2.6	2.9	0.6	—
2.2	21.3	11.2	10.5	0.2	0.4	1.2	0	n-C_4F_{10} (0.2)
3.3	23.4	19.9	24.0	0	1.0	1.1	0	CCl_2FCClF_2 (1.1)
4.2	0.7	1.1	0	0.3	2.8	1.4	1.2	$CHClF_2$ (0.9) n-C_4F_{10} (0.7)
7.6	0	2.2	0	0.8	3.0	4.6	0	CCl_2FCClF_2 (1.1) $CHClF_2$ (3.8)

by the mole of starting material fed. The yield shown in other tables was calculated with the similar way.

$$CH_3CH_3 + 11F + Cl = C_2ClF_5 + 6HF \text{ (11 Farady)}$$

efficiency shown in other tables was calculated with the similar way to these examples.

WITH METHANE

composition, %				
CCl_2F_2	$CHCl_2F$	CH_2ClF	CH_3Cl	Others, %
2.5	0.6	7.2	22.1	CH_3F (10.9), CF_3CF_3 (0.3), CH_3CF_3 (1.2)
13.1	3.1	6.9	13.8	CCl_3F (1.5)

ETHYLENE, ETHANE AND FLUOROETHYLENE

fluoride systems)

He, 40 m*l*/min; NaF 10 g; CCl_4, 0.426 mol; $CHCl_3$, 0.567 mol; anodic current density, 2.2

16°C (runs 10, 11, 12 and 13).

composition, %									
CHF_2CHF_2	CHF_2CClF_2	$CClF_2CClF_2$	CH_3CF_3	CH_2FCClF_2	CH_3CClF_2	CHF_3	CH_2F_2	$CHClF_2$	$CHCl_2F$
16.5	6.4	1.8	24.0	0	0	3.2	0	4.6	3.0
9.3	9.6	3.5	15.3	14.9	3.2	2.7	3.7	2.1	5.1
7.8	4.7	1.2	29.9	8.9	12.3	1.5	0	1.6	3.2
6.9	27.9	7.9	3.4	1.0	0	5.4	4.2	5.4	5.1
15.9	8.8	0.7	44.6	5.4	—	—	—	—	—

11 and 12, and those from chloroform in run 13 were not considered in the calculation of yield, current

Experimental

Materials. Ethylene (99.0% min), ethane (99.7%), and methane (99.9%) were obtained from the Takachiho Chemical Industrial Co., and fluoroethylene (99.9%), from the Matheson Co. Anhydrous hydrogen fluoride was of a commercial grade (Daikin Industries Co.); it was used as has previously been described.[9] The other common reagents were either of a guaranteed or of a commercial grade.

Apparatus. Electrolytic cells of two different sizes and design were employed. The runs using chlorine or phosgene as the chlorinating agent were performed in an iron cell (type A), 300 m*l* in capacity, which was circular in cross section (6 cm in diameter). The electrodes consisted of a pack of alternate anodes (8 nickel sheets) and cathodes (7 nickel sheets), fastened together, but insulated from each other. The effective surface area of the anodes was 7.7 dm². The cell was provided with a reflux condenser (of copper), with brine circulating through, (−25°C) and with a cooling mantle filled with ice water. The bubbler in the cell was made similarly to the one described in a previous paper.[9]

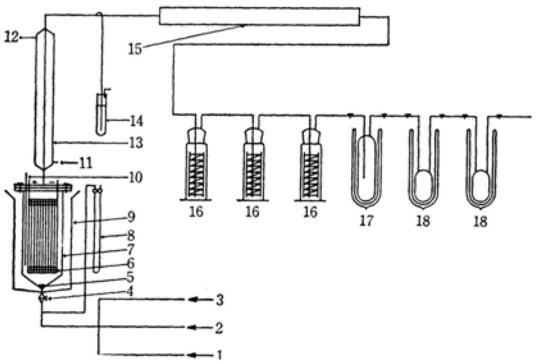


Fig. 1. Schematic diagram of apparatus.

1. Chlorine inlet
2. Helium inlet
3. Sample inlet
4. Cock
5. Bubbler
6. Electrodes
7. Cell body
8. Pressure indicator
9. Cooling mantle
10. Thermometer well
11, 12. Coolant inlet and outlet
13. Reflux condenser
14. Safety valve
15. Hydrogen fluoride absorber
16. Oxygen difluoride and chlorine absorber
17. Trap (ice)
18. Trap (liquid nitrogen)

A schematic diagram of the apparatus, including the cell, hydrogen fluoride absorber (an iron pipe containing sodium fluoride pellets), oxygen difluoride and chlorine absorber (gas washing bottles covered an aqueous solution of sodium sulfite with sodium hydroxide and potassium iodide), and a series of cold traps, is shown in Fig. 1. The mercury in the safety valve and in the pressure indicator was covered by fluorocarbon oil to protect it from chlorine.

The runs using carbon tetrachloride or chloroform as the source of chlorine were carried out in a cell (type B) which was the same as that used earlier.9)

The other instruments (a low-temperature distillation unit, and an infrared spectroscopic apparatus) were the same as those described before.9) Chromatographic separation was made with a Shimadzu GC-1C model chromatograph, equipped with a silica-gel column, using helium as the carrier gas.

Procedures. A typical procedure for the runs in the A-type cell was as follows. Ethylene (20 m*l*/min), chlorine (10 m*l*/min), and helium (25 m*l*/min) were directed from the respective cylinders through the bubbler into 300 m*l* of hydrogen fluoride containing 5 g of the conductivity additive (sodium fluoride), while the current was being passed through with the anodic current density of 1.7 A/dm^2, at the cell voltage of 6.6 V, and at the cell temperature of 11°C. Helium was used as a diluent to avoid an explosion; it also aided the agitation of hydrogen fluoride. When the reaction system became steady (after about 1 hr of electrolysis), ice and liquid nitrogen were placed in the respective cold traps, and the electrolysis was carried out for 26 A·hr. The gases evolved from the cell were passed through the sodium fluoride, bubbled through the absorber for oxygen difluoride and chlorine, and then trapped in glass tubes immersed in the cold bath. Hydrogen gas was allowed to escape into the air.

The procedure and method for the identification of the products were similar to those described previously:9,10) molecular-weight measurement, followed by gas chromatographic and infrared spectroscopic analyses. Except for 1-chloro-1, 1-difluoroethane, the compounds identified in the present experiment were the same as those obtained in the previous works.1,2,9,10) The authentic sample of 1-chloro-1, 1-difluoroethane was prepared from 1, 1, 1-trichloroethane by fluorination with antimony trifluoride in the presence of antimony pentachloride.12)

The procedure for the runs in the B-type cell was essentially the same as that illustrated above, but the features of the reaction were different. In this case, a gaseous mixture of the sample and helium was introduced into 1 *l* of hydrogen fluoride containing 10 g of dissolved sodium fluoride and chlorohydrocarbon (carbon tetrachloride, 0.426 mol, or chloroform, 0.567 mol), which is not miscible with hydrogen fluoride;11) thus, the gases first passed through the organic layer and then through the hydrogen fluoride layer.

The principal products obtained were similar to those obtained from the chlorine - hydrogen fluoride system. In run 11, hexachloroethane (4 g) was extracted with ether from the residue in the cell after the distillation of the bulk of the hydrogen fluoride.

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12) A. L. Henne and M. W. Renoll, *J. Am. Chem. Soc.*, **58**, 889 (1936).