The Fluorination of Chloromethane, Chlorodifluoromethane and Dichlorofluoromethane*

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The previous papers in this series[1,2] have shown that organic gases which are not very soluble in hydrogen fluoride can be fluorinated controllably by electrochemical fluorination. A good deal has been learned about the electrochemical fluorination of liquid halogenohydrocarbons, including unsaturated ones,[3-8] but no detailed report has yet been made on gaseous compounds.[9]

This paper will deal with the electrochemical fluorination of chloromethane. Such halogenomethanes as chlorodifluoromethane and dichlorofluoromethane were also fluorinated for the sake of comparison.

Chloromethane yielded all the expected fluorinated methanes (tetrafluoromethane, chlorotrifluoromethane, trifluoromethane, chlorodifluoromethane, difluoromethane, chlorofluoromethane and monofluoromethane) in a substantial total yield and with reasonable current efficiency. Chlorination reaction took place to a slight extent during the fluorination, giving traces of dichlorodifluoromethane and dichlorofluoromethane.

Tetrafluoromethane, chlorotrifluoromethane, and trifluoromethane were formed from chlorodifluoromethane, and tetrafluoromethane, chlorotrifluoromethane, trifluoromethane, dichlorodifluoromethane, and chlorodifluoromethane, from dichlorofluoromethane, in reasonable total yields, but with low current efficiencies.

The reaction conditions used for respective samples and the results obtained are summarised

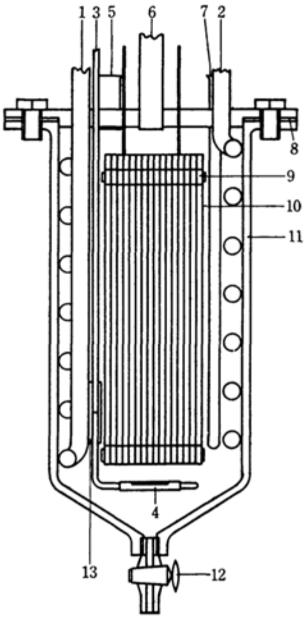

Fig. 1. Electrolytic fluorination cell and bubbler.

1, 2	Inlet and outlet of cooling spiral for temperature regulation
3	Sample feed tube
4	Bubbler
5	Inlet for sodium fluoride addition
6	Lowest part of reflux condenser
7	Thermometer well
8	Neoprene packing
9	Polytetrafluoroethylene spacers between anodes and cathodes
10	Electrodes
11	Cell body
12	Valve for draining
13	Polyethylene tube connector

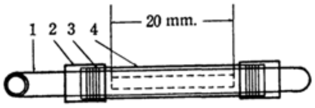

Fig. 2. Bubbler.

1	Copper tube
2	Polyethylene sheet
3	Copper wire
4	Polytetrafluoroethylene filter paper

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* "The Electrochemical Fluorination of Gases," Part III. Presented in part at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

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TABLE I. THE FLUORINATION OF CHLOROMETHANE[a)]

Run No.	Sample[b)] feed rate ml./min.	Total amount of sample fed mol.	Electricity passed amp. hr.	NaF used g.	He used ml./min.	Temp. °C	Total[c)] yield mol.%	Total[d)] current eff. %
1	30	0.448	111	10	0	5—6	85.4	45.2
2	52	0.607	86	10	0	5—6	61.5	52.5
3	71	0.482	49	10	0	5—6	36.5	41.1
4	52	0.525	76	50	0	5—6	50.2	32.4
5	52	0.527	76	10	104[e)]	5—6	74.7	56.1
6	52	0.502	70	10	0	—10[f)]	33.1	27.8
7	52	0.568	80	10	0	16	75.0	76.6

Run No.	Product compn., mol.%						
	CF_4	$CClF_3$	CHF_3	$CHClF_2$	CH_2F_2	CH_2ClF	CH_3F
1	18.3	13.2	35.2	17.0	8.7	4.4	3.2
2	15.5	11.2	25.3	20.1	15.4	7.8	4.7
3	17.2	10.5	22.0	12.5	10.7	19.9	7.2
4	7.7	2.2	16.4	22.6	17.6	20.8	12.7
5	6.0	5.2	37.5	14.9	19.3	7.5	9.6
6	14.6	6.5	35.4	11.6	18.4	4.5	9.0
7	13.6	6.7	22.9	22.0	17.6	6.9	10.3

a) All the experiments were carried out with the anodic current density of 2.2 amp./dm².

b) Gas volume is expressed in normal condition in this table and in Table II.

c) Calculation of yield of fluorinated product was based on the amount of CH_3Cl fed. A trace of chlorinated by-products, CCl_2F_2 and $CHCl_2F$ was neglected in quantitative calculation.

d) Total current efficiency shown was the sum of the current efficiency of each component based on the following equations, ($n=1, 2,$ or 3).

$$CH_3Cl + 2nF = CH_{3-n}F_nCl + nHF \quad (1)$$

$$CH_3Cl + (2n+1)F = CH_{3-n}F_{n+1} + nHF + Cl \quad (2)$$

e) Dilution ratio (CH_3Cl : He) is 1 : 2 by volume.

f) The cell temperature was raised to 6°C at the end of the reaction.

TABLE II. THE FLUORINATION OF CHLORODIFLUOROMETHANE AND DICHLOROFLUOROMETHANE[a)]

Run No.	Sample feed rate ml./min.	Total amount of sample fed mol.	Electricity passed amp. hr.	Temp. °C	Total[b)] yield mol.%	Total[c)] current eff. %	Product compn., mol. %				
							CF_4	$CClF_3$	CHF_3	CCl_2F_2	$CHClF_2$
					Chlorodifluoromethane						
1	27	0.410	117	5—6	55.4	12.6	58.4	24.6	17.0		
2	52	0.502	70	5—6	43.2	19.4	48.0	37.3	14.7		
3	69	0.580	58	5—6	42.6	24.9	33.4	52.0	14.6		
4	52	0.502	68	—10[d)]	48.3	14.5	8.4	33.8	57.8		
5	52	0.404	57	—2[d)]	53.8	19.0	21.0	42.1	36.9		
6	52	0.502	70	12—13	49.1	21.5	44.6	38.2	17.2		
					Dichlorofluoromethane[e)]						
1	23	0.240	77	5—6	76.0	15.5	23.1	12.4	1.7	49.0	13.8
2	55	0.239	32	5—6	60.6	26.1	12.5	11.2	6.9	51.9	17.5
3	56	0.240	33	—9[d)]	37.6	14.5	1.2	12.0	18.4	49.2	19.2
4	55	0.155	21	10	59.5	27.9	18.9	12.6	1.8	55.3	11.4

a) All the experiments were carried out with the anodic current density of 2.2 amp./dm², with the addition of 10 g. of NaF.

b) Calculation of yield was based on the amount of $CHClF_2$ and $CHCl_2F$ fed, respectively.

c) Calculation of the current efficiency was made with the similar way to that for chloromethane.

d) The cell temperature was raised to 6°C at the end of the reaction.

e) This was introduced together with the carrier of helium (rate at 35 ml./min.) into the cell through the bubbler.

n Tables I and II. It is apparent that the milder fluorination reaction proceeded with an increased sample feed rate, as has also been observed in the fluorination of methane[1] and of ethylene and ethane[2].

Helium appeared to serve satisfactorily as a diluent, and the addition of an increased amount of sodium fluoride resulted in a milder reaction in chloromethane.

The total yield and the current efficiency, as well as the composition of the products, were much affected by the electrolysis temperature.

The order of the facility of replacement between hydrogen and chlorine by fluorine seemed to be indefinite in chloromethane under the fluorination conditions used. In chlorodifluoromethane, the replacement of hydrogen was usually favored over the replacement of chlorine; it yielded a larger amount of chlorotrifluoromethane than that of trifluoromethane.

At lower temperatures, however, this apparent relation was reversed. A similar tendency was observed in dichlorofluoromethane.

Experimental

Apparatus.—Fluorination units, which mainly consisted of an electrolytic cell (1 l. in capacity), a safety tube dipped in mercury, a hydrogen fluoride absorber, an oxygen difluoride absorber, and condensing traps, were virtually identical with those described earlier,[1] but the position of the bubbling arrangement (the bubbler) in the cell and its shape were modified, as is illustrated in Figs. 1 and 2 respectively.

Figure 1 shows a sectional view of the cell with the bubbler, while the plan of the bubbler is shown in Fig. 2. The bubbler consisted of an L-shaped copper tube about 100 mm. in total length and 4 mm. in diameter. At the horizontal portion (about 60 mm. in length) of the tube, a slit-like hole of 2×20 mm. was opened toward the direction of the lower end of the nickel electrodes (the effective surface area of the electrodes was 9.2 dm^2). The hole was wrapped with a filter paper made of polytetrafluoroethylene fiber (Daikin Industries Co.), which was fixed with a copper wire and a polyethylene sheet. The distance between the hole and the lower end of the electrodes was about 8 mm. One end of the copper tube was closed, while the other end was connected to the sample feed tube.

The sample introduced through the sample feed tube was led to the bubbler and came out as a number of minute bubbles in hydrogen fluoride.

Materials and Procedure.—Chloromethane (99.5 %) was obtained from the Matheson Co. Chlorodifluoromethane and dichlorofluoromethane from a commercial cylinder were used after purification by distillation.

The operating procedures used in the fluorination were essentially the same as those described previously.[2] Low-temperature distillation and gas chromatography (a silica gel column was employed) were used for the quantitative analysis of the products. Infrared measurements were frequently carried out in order to identify the components.