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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

## Synthesis of Perfluoroalkanes by High-Temperature Reaction of Graphite with Fluorine in a Fluidized Bed

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Abstract—Synthesis of lower perfluoroalkanes (tetrafluoromethane, hexafluoroethane, octafluoropropane, decafluorobutane) by high-temperature reaction of graphite with fluorine in a fluidized bed was studied.

Tetrafluoromethane, hexafluoroethane, octafluoropropane, and decafluorobutane are widely used in the modern industry as ozone-friendly refrigerants, propellants, dielectrics, and gas-phase fluorine carriers for semiconductor industry [1]. The annual world consumption of these substances reaches several thousand tons; therefore, development of efficient processes for their production is an urgent problem.

There exist several procedures for preparing these compounds. Tetrafluoromethane is prepared from the elements in the inverse wave of filtration combustion of graphite in fluorine, using a fixed graphite bed [2]. The feasibility parameters of this process are high.

Hexafluoroethane can be prepared by catalytic fluorination of fluorochloroethanes with HF [3]. The raw materials for these process destroy the ozone layer, and their production should be stopped. The process has also other drawbacks: large amount of hydrogen chloride waste and the necessity of regeneration and utilization of the environmentally hazardous chromium magnesium fluoride catalyst.

Octafluoropropane is produced by fluorination of hexafluoropropylene with cobalt trifluoride [4]. The production of hexafluoropropene also involves ozonedecomposing substances [1]. Furthermore, processes involving cobalt trifluoride as fluorinating agent have low productive capacity.

Decafluorobutane can be prepared by electrochemical fluorination of tributylamine in an HF solution [5]. However, the yield and productive capacity of the process are poor.

At the same time, it is known that all the above perfluorocarbons and solid carbon polyfluoride  $(CF_x)_n$ 

are formed by high-temperature reaction of carbon with fluorine:

$$C(s) + F_2(g) \rightarrow (CF_x)_n(s) + CF_4(g) + C_2F_6(g) + C_3F_8(g) + C_4F_{10}(g) + \dots$$
(1)

The boiling points of tetrafluoromethane, hexafluoroethane, octafluoropropane, and decafluorobutane are -128, -78, -37, and  $-2^{\circ}$ C, respectively. In industrial implementation of reaction (1), separation of the products by distillation seems to involve no serious problems. Thus, commercial mastering of carbon fluorination will allow several different processes to be combined in a single process involving simple and cheap raw materials, with an efficient distillation system.

Published data on the composition of gaseous products of carbon fluorination are contradictory. However, most of the authors indicate that the major product is tetrafluoromethane. As an efficient process for tetrafluoromethane production has been commercially mastered [2], development of the process based on carbon fluorination is appropriate only if higher fluoroalkanes will be obtained in a yield comparable with that of  $CF_4$ .

Moissan was the first to perform the reaction of carbon with fluorine [6]; he found that amorphous carbon forms ignite in fluorine even at room temperature, whereas graphite and diamond are resistant to fluorine at normal temperature. Ruff reported in 1934 [7] that at 420°C graphite reacts with fluorine to form a solid compound, carbon polyfluoride  $(C_xF_y)_n$ . He also found that at 460–700°C the reaction occurs with explosion, and at temperatures above 700°C graphite burns in fluorine to form fluorocarbons, mainly tetra-



**Fig. 1.** Scheme of the reactor: (1) reactor body, (2) tube for feeding the fluorinating mixture, (3) chamber for separation of the gas and powder, (4) reactor lid, and (5) filter; (H<sub>1</sub>, H<sub>2</sub>) electric heaters, (T<sub>1</sub>-T<sub>5</sub>) thermocouples for the medium, and (Tc<sub>1</sub>-Tc<sub>2</sub>) thermocouples for the walls.

fluoromethane [8]. It was shown later [9] that the composition of carbon polyfluoride depends on the synthesis temperature and graphite particle size. Later, numerous papers concerning preparation of carbon polyfluoride were published; its composition, structure, properties, fluorination kinetics, and application fields were studied. Carbon polyfluoride found use as a solid lubricant and a cathodic material for lithium cells [10].

Thus, the majority of papers on fluorination of carbon were devoted to properties of carbon polyfluoride and procedures for its production; perfluoroalkanes were considered as by-products [11–13]. The available data are insufficient to determine the optimal conditions for preparing hexafluoroethane, octafluoropropane, and decafluorobutane from carbon and fluorine.

The goal of this study was to find conditions of carbon fluorination ensuring formation of a mixture of perfluoroalkanes containing tetrafluoromethane, hexafluoroethane, octafluoropropane, and decafluorobutane in commercially significant amounts.

The reaction of fluorine with carbon is strongly exothermic; in formation of  $CF_4$ , the thermal effect is 933 kJ mol<sup>-1</sup>. The temperature of the reaction products in the adiabatic mode reaches several thousand degrees. Under these conditions, hexafluoroethane, octafluoropropane, and decafluoroethane decompose with the formation of other fluorocarbons, fluorine, and carbon.

To ensure the stability of the target products under the synthesis conditions, it is necessary to efficiently remove the released heat. This can be done by using dynamic (agitated) beds of powdered carbon.

Fluidization is one of the most advanced procedures for performing heterogeneous processes involving a solid phase. Systems fluidized with a gas flow are characterized by strong agitation inside the bed, provided by ascending gas "bubbles" [14]. Owing to the large surface area of solid particles, the heat exchange between them is very intense, and the difference between the temperatures of the fluidizing agent and solid particles is very small. To ensure stable fluidization, it is appropriate to use friable powders showing no tendency to sinter. Therefore, for laboratory tests we chose electrode graphite as a carbon material.

## EXPERIMENTAL

For visual monitoring of the fluidization, experiments were performed in a model glass reactor. Stable fluidization without separation and removal of the particles is observed with the graphite fraction with the particle size less than 250  $\mu$ m at a fluidizing gas velocity less than 15–20 cm s<sup>-1</sup>. The contact time of the gas and powder varies from 0.5 to 3 s depending on the fixed bed height.

For fluorination experiments, we constructed a laboratory installation with a reactor containing a fluidized graphite bed. The reactor (Fig. 1) was a thick-walled pipe I from carbon steel of the following size: internal diameter 12 mm, external diameter 45 mm, and height 500 mm. The fluorinating mixture is fed through a porous insert 2 from pressed nickel powder, arranged in the bottom part of the pipe. In the top part, the pipe has an expansion 3 28 mm in diameter for decreasing the gas velocity and separating the graphite particles. A filtering gauze is arranged at the reactor outlet.

To maintain the required temperature, two electric

<i>T</i> , °C	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	C <sub>2</sub> F <sub>4</sub>	C <sub>3</sub> F <sub>8</sub>	C <sub>3</sub> F <sub>6</sub>	C <sub>4</sub> F <sub>10</sub>	Σς /ς	
		$2 S_{\rm CF}/S_{\rm N}$						
410	49.9	16.8	_	18.2	_	15.1	0.018	
425	50.8	18.1	_	18.8	_	12.3	0.019	
450	44.7	20.2	_	20.4	_	14.7	0.024	
460	53.8	15.9	_	15.9	_	14.4	0.019	
465	57.7	15.5	_	16.4	_	10.4	0.026	
490	62.4	17.1	_	15.1	_	5.4	0.017	
495	63.8	17.1	0.2	13.0	_	6.0	0.074	
520	64.0	17.3	0.1	13.8	_	4.8	0.075	
540	64.1	17.7	_	14.7	0.5	3.0	0.080	
560	63.6	15.2	_	13.6	1.5	6.2	0.084	
585	58.2	21.2	_	13.6	1.2	5.8	0.081	
590	59.1	19.2	_	13.5	1.5	6.7	0.084	
610	62.9	20.8	_	11.2	1.5	3.6	0.088	
635	66.2	22.0	_	8.3	1.5	2.0	0.084	
670	70.2	19.8	_	7.0	1.6	1.4	0.090	
720	75.9	14.2	=	7.3	1.1	1.5	0.092	

Table 1. Composition of gaseous products of the reaction of fluorine with graphite in the steady-state isothermal mode as influenced by temperature. Contact time 3 s, fluorinating mixture 20%  $F_2$  + 80%  $N_2$ 

heaters  $H_1$  and  $H_2$  are mounted on the reactor surface. The wall temperature is monitored with Chromel– Alumel thermocouples  $Tc_1$  and  $Tc_2$ . The thermocouples in two-channel ceramic straws are arranged in wells 8 mm deep and 3 mm in diameter, so as to ensure reliable thermal contact between the thermocouple junction and well bottom.

The temperature of the reaction medium in the reactor volume is measured with Chromel–Alumel thermocouples  $T_1-T_5$ . The distance from the  $T_1$  junction to the gas-feeding surface is 15 mm, and the distance between the junctions of the thermocouples, 115 mm.

As a fluidizing gas we used a mixture of fluorine and nitrogen, and as a carbon material, electrode graphite with the particle size less than 250  $\mu$ m.

The expansion of the graphite powder bed was monitored with thermocouples  $T_1-T_5$ . If the bed expanded to occupy the whole channel height, the temperature became virtually equal throughout the reacting bed.

The experiment time was 25–30 min. In this time, the temperature of the reactor wall increased by no more than 15°C. Thus, fluorination of graphite was performed under approximately isothermal conditions.

Chromatographic analysis of the gaseous reaction products showed that the composition of the products changed during the first 5 min of the reaction. In the subsequent period, at constant feed rate and temperature, the composition of the gaseous products was stable and could be averaged.

The averaged (over the samples taken) composition of the gaseous products of the reaction of fluorine with graphite in the steady-state isothermal mode is given in Table 1 for various temperatures. At each temperature, we took three to five samples. When calculating the sample composition, we assumed the chromatographic correction coefficients to be unity for all the substances.

In Table 1 we also give the parameters  $\Sigma S_{CF}/S_N$  characterizing the content of gaseous fluorocarbons in the gas flow. The parameter  $\Sigma S_{CF}/S_N$  is the ratio of the total area of the fluorocarbon chromatographic peaks to the nitrogen peak area. The fluorine break-through was detected only at 410°C.

The dependence of the parameter  $\Sigma S_{CF}/S_N$  on the fluorination temperature (contact time 3 s) is shown in Fig. 2.

Using the parameter  $\Sigma S_{CF}/S_N$ , we can qualitatively estimate the amount of fluorine consumed for formation of gaseous perfluorocarbons and solid carbon polyfluoride. This allows comparison of the rates of the synthesis and thermal decomposition of carbon polyfluoride and estimation of the accumulation of carbon polyfluoride in the reactor.

The molar ratio of fluorine and carbon in the gase-

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**Fig. 2.** Parameter  $\Sigma S_{CF}/S_N$  as a function of temperature *T* at a gas-powder contact time of 3 s: (1) experimental dependence, (2) theoretical value corresponding to formation of CF<sub>3.2</sub> (which corresponds to the average composition of products obtained at 580–600°C), and (3) theoretical value corresponding to formation of CF<sub>4</sub>.

ous reaction products at  $550-600^{\circ}$ C was 1:3.2 (Table 1).

Thus, the volume of gaseous fluorocarbons is by a factor of 3.2 smaller than the volume of fluorine consumed for their formation. The feed contained 20% fluorine, and the ratio of the volume of the gaseous reaction products to the volume of nitrogen,  $\Sigma S_{CF}/S_N$ , at a temperature close to 580°C should be

$$\frac{\sum S_{\rm CF}}{S_{\rm N}} = \frac{20/3.2}{80} = 0.078.$$

At 400–450°C, the theoretical value of  $\Sigma S_{CF}/S_N$  is 0.083.

If the only fluorination product were tetrafluoromethane, the  $\Sigma S_{CF}/S_N$  ratio would be the following:

$$\frac{\sum S_{\rm CF}}{S_{\rm N}} = \frac{20/2}{80} = 0.125$$

At 400–450°C, the experimental value of  $\Sigma S_{CF}/S_N$  is lower than the theoretical value by a factor of 4. This means that the fluorine fed into the reactor does not fully leave the reactor in the form of gaseous

**Table 2.** Composition of gaseous products of the reaction of fluorine with graphite as influenced by temperature. Contact time 0.6 and 0.8 s

<i>T</i> , °C	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	$C_2F_4$	$C_3F_8$	C <sub>3</sub> F <sub>6</sub>	$C_4F_{10}$		
	vol %							
565 590	59.2 62.3	20.9 17.9	1.6 _	11.8 13.3	1.3 1.0	5.2 5.4		

compounds. Hence, at this temperature the rate of formation of carbon polyfluoride is higher than the rate of its decomposition, and carbon polyfluoride accumulates in the reactor.

At temperatures above 550°C, the experimental  $\Sigma S_{CF}/S_N$  value agrees with the theoretical value; hence, the fluorine fed into the reactor fully leaves the reactor in the form of gaseous products. A slight increase in  $\Sigma S_{CF}/S_N$  at temperatures exceeding 550°C is associated with an increase in the CF<sub>4</sub> content in the reaction products.

Thus, the gaseous products of graphite fluorination in a fluidized bed under the optimal conditions (550– 600°C), when the CF<sub>4</sub> content is minimal and carbon polyfluoride does not accumulate, have the following composition (wt %): 40–45 CF<sub>4</sub>, 20–25 C<sub>2</sub>F<sub>6</sub>, 20–25 C<sub>3</sub>F<sub>8</sub>, and 10–15 C<sub>4</sub>F<sub>10</sub>.

To estimate the minimal time of complete conversion of fluorine in a fluidized bed, we performed experiments with shorter contact times of the gas and powder: 0.6 and 0.8 s. The results are given in Table 2. No breakthrough of fluorine was observed. The composition of the gaseous products did not noticeably differ from that obtained at a contact time of 3 s.

Table 1 and Fig. 2 suggest that formation of gaseous perfluorocarbons involves intermediate formation of carbon polyfluoride, followed by its decomposition. To check this assumption, we performed experiments on synthesis and thermal decomposition of carbon polyfluoride. Carbon polyfluoride was prepared at  $400-500^{\circ}$ C in a fluidized bed for 35-40 min. The composition of carbon polyfluoride after the fluorination corresponded to the formula (CF<sub>0.30-0.35</sub>)<sub>n</sub>.

Then we stopped the supply of gaseous fluorine and performed the decomposition at a higher temperature in a nitrogen flow ensuring fluidization and isothermal conditions. The decomposition of carbon polyfluoride was performed for approximately 10-100 min.

The composition of the gaseous products of thermal decomposition of carbon polyfluoride is given in Table 3.

These data confirm the assumption that perfluorocarbons containing more than one carbon atom are formed by synthesis and decomposition of carbon polyfluoride.

Tables 3 and 1 show that, as x in  $(CF_x)_n$  decreases, the yield of tetrafluoromethane in decomposition of  $(CF_x)_n$  increases. Also, the yield of tetrafluoromethane

Run no.	τ, min	T, °C	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	C <sub>3</sub> F <sub>8</sub>	C <sub>3</sub> F <sub>6</sub>	C <sub>4</sub> F <sub>10</sub>	$\sum S = /S$
				$2 S_{\rm CF}/S_{\rm N}$				
1	11 19 22 25 29 14	555 590 600 620 635 560	68.3 70.2 77.7 81.6 86.5 73.1	19.3 20.8 14.4 14.9 13.5 14.8	6.6 5.6 5.1 3.5 0.0 8.4	3.2 2.0 2.8 - 1.7	2.6 1.4 - - 2.1	- - - - -
	19 22	600 620	74.0 81.0	17.2 14.2	5.5 4.9	2.2	1.1	_
3	9 23 35 51 61 80 92 102	465 465 465 465 530 570 580	75.4 77.8 76.8 75.9 78.0 74.0 75.5 86.7	11.7 11.7 10.5 10.6 11.4 15.0 15.8 7.9	12.9 10.5 9.1 6.9 6.4 7.1 6.0 3.7	- 3.6 4.4 4.2 2.3 2.7 1.7	_ _ 2.2 _ 1.6 _	$\begin{array}{c} 0.016\\ 0.016\\ 0.017\\ 0.015\\ 0.015\\ 0.205\\ 0.036\\ 0.013\\ \end{array}$
4	13.5 16.5 23.5 35.5 54.5 69.5 77.5	478 504 540 546 562 566 568	62.7 69.2 73.1 75.0 82.1 88.5 82.0	16.9 12.8 15.3 15.1 9.9 8.1 12.3	14.4 13.4 7.1 6.0 2.7 3.3 3.9	1.5 2.3 3.2 2.5 0.1 1.5	6.0 3.1 2.1 0.7 2.8 - 0.3	$\begin{array}{c} 0.016 \\ 0.105 \\ 0.133 \\ 0.033 \\ 0.010 \\ 0.004 \\ 0.004 \end{array}$
5	12 21 27 31	530 590 620 630	73.5 71.9 82.9 85.4	13.4 17.8 10.8 11.7	8.8 6.2 2.7 2.9	2.0 2.3 3.6	2.3 1.8 _	0.051 0.141 0.018 0.020

**Table 3.** Composition of gaseous products of thermal decomposition of carbon polyfluoride in a fluidized bed as influenced by the reaction temperature and time. Nitrogen flow rate  $6 \text{ cm}^3 \text{ s}^{-1}$ 

is higher in decomposition of  $(CF_x)_n$  prepared in advance (Table 3) than in synthesis–decomposition of  $(CF_x)_n$  at the same temperature (Table 1). These facts suggest the following.

When a graphite particle reacts with fluorine, a film of carbon polyfluoride with high x is formed on the particle surface, whereas the internal region of the particle remains unchanged. The lowest yield of tetra-fluoromethane was observed in thermal decomposition of the film with a high x. If the film does not decompose rapidly and the particle occurs for a long time at approximately 500°C, the fluorine inside the particle is redistributed, i.e., the two-layer distribution pattern with  $x \rightarrow 1$  at the surface and  $x \rightarrow 0$  inside the particle changed for a uniform distribution of fluorine with a constant x throughout the particle volume. In thermal

decomposition of such a sample of carbon polyfluoride ( $x \ll 1$ ), the yield of CF<sub>4</sub> is high.

Thus, to decrease the yield of  $CF_4$ , it is appropriate to perform the thermal decomposition of the synthesized carbon polyfluoride as quickly as possible, so as to avoid equalization of x throughout the particle volume.

We performed experiments on fluorination of graphite in a fluidized bed using a fluorinating mixture with an increased fluorine concentration. The results are listed in Table 4. The temperature measurements showed that the fluorination occurred in the isothermal mode; no fluorine breakthrough occurred.

Comparison of Tables 1 and 4 shows that, as the fluorine concentration in the fluorinating mixture is

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**Table 4.** Composition of gaseous products of reaction of fluorine with graphite in the steady-state mode as influenced by temperature. Contact time 3 s, fluorinating mixture composition 40% F<sub>2</sub> + 60% N<sub>2</sub>

<i>T</i> , °C	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	$C_2F_4$	C <sub>3</sub> F <sub>8</sub>	C <sub>3</sub> F <sub>6</sub>	C <sub>4</sub> F <sub>10</sub>		
	vol %							
580 590	75.43 75.65	13.9 14.18	0.02 0.06	7.37 6.72	0.57 0.4	2.49 2.99		

increased, the product composition changes: the amount of  $CF_4$  increases, and that of the other fluoro-carbons decreases.

This experimental fact can be explained as follows. Two reaction zones can be distinguished in the reaction unit: the zone of the fluorine uptake in which solid carbon polyfluoride is formed and the zone of the carbon polyfluoride decomposition yielding gaseous perfluorocarbons. In a reactor with a circulating fluidized bed, the zone of decomposition of carbon polyfluoride occupies the whole reactor volume, whereas the zone of formation of carbon polyfluoride occupies only its part. These zones overlap (Fig. 3), and thermal decomposition of carbon polyfluoride occurs in a medium containing gaseous fluorine.

As the fluorine concentration in the fluorinating mixture is increased, the height of the zone of the fluorine uptake increases. Apparently, under the experimental conditions the gaseous fluorocarbons react with fluorine to give lower-molecular-weight perfluoro compounds. Therefore, at increased fluorine content in the fluorinating mixture, the yield of  $CF_4$  is higher.

Thus, to increase the yield of perfluorocarbons containing more than one carbon atom, it is appropri-



**Fig. 3.** Scheme of the distribution of the reaction zones in the reactor channel: (1) zone of fluorine uptake and (2) zone of decomposition of carbon polyfluoride. Fluorine concentration, %: (a) 20 and (b) 40.

ate to perform the decomposition of the synthesized polyfluoride in the absence of fluorine in the decomposition zone.

## CONCLUSIONS

(1) The major gaseous products of graphite fluorination are  $CF_4$ ,  $C_2F_6$ ,  $C_3F_8$ , and  $C_4F_{10}$ ; the amounts of  $C_2F_4$  and  $C_3F_6$  do not exceed 2.0 wt %.

(2) At 550–600°C, the composition of the reaction products is as follows (wt %): 40–45 CF<sub>4</sub>, 20–25 C<sub>2</sub>F<sub>6</sub>, 20–25 C<sub>3</sub>F<sub>8</sub>, and 10–15 C<sub>4</sub>F<sub>10</sub>.

(3) Synthesis of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, and C<sub>4</sub>F<sub>10</sub> involves intermediate formation of  $(CF_x)_n$  followed by its thermal decomposition.

(4) At temperatures above 550°C, solid carbon polyfluoride does not accumulate in the laboratory reactor.

(5) To increase the yield of perfluorocarbons containing more than one carbon atom, it is appropriate to perform the decomposition of  $(CF_x)_n$  with  $x \to 1$ under the isothermal conditions in the absence of fluorine.

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