

PECULIARITIES OF BrF₃ INTERCALATION INTO OXIDIZED GRAPHITE

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ABSTRACT

At interaction of graphite oxides (OG) of different degrees of oxidation with bromine trifluoride, graphite fluoroxides were obtained with general composition C₈O_xF_y, where indices x and y were determined by the C/O ratio in the initial graphite oxide. Properties of the compounds obtained were studied by means of the ¹⁹F NMR method, IR-spectroscopy, DTA, ESCA and X-ray diffraction. The described method for synthesis of graphite fluoroxides (FOG) allowed us to divide the product into two phases, different in their hydrophilic properties. It was shown that OG fluorination by bromine trifluoride does not involve matrix carbonyl, therefore, OG capability for fluorination decreased at decrease of C/O ratio.

INTRODUCTION

Several reports of synthesis and properties of graphite fluoroxides appeared in the literature. According to Lagow et al. [1] FOGs were formed at fluorination of graphite oxide with gaseous fluorine at room temperature. FOGs contained 16-22% of F which decomposed at t > 50°C and were unstable if kept in humid air. Nazarov et al. [2] reported the existence of hydrolytically stable FOG containing 30-50% of fluorine and thermostable up to 300°C. They were obtained by fluorination of OG with solutions of K₂NiF₆ in fluoric hydrogen in the range of 20-100°C. FOG of a new structure was obtained at fluorination of OG by elementary fluorine at 100°C [3]. The present paper studies a relation between the degree of oxidation of the initial oxygen-containing matrix and composition and properties of FOGs obtained.

EXPERIMENT

Initial series of OG were obtained by oxidation of natural graphite (30g) with particle sizes of about 50µm with potassium permanganate in a mixture of 96% sulphuric and 68% nitric acids. The amount of the oxidizer was gradually increased from 0.5 to 100g (Table 1) and added which mixing and cooling the reaction mixture during several days. Next day, the products were hydrolyzed at 100°C. Isolation of OGs was conducted by means of centrifugation and successive washing with nitric and hydrochloric acids, then with water to pH=7. The OGs obtained were dehydrated on teflon filter

under pressure of inert gas, then were washed by hydrofluoric acid and gaseous fluorine to prepare the samples for fluorination.

Fluorination was carried out with BrF_3 in a teflon reactor at room temperature adding OG until dense homogeneous mass coloured green formed. In order to attain maximum homogeneity of the products, the system was kept for 30 days. After opening the reactor, the FOGs were hydrolyzed in water excess. At hydrolysis of BrF_3 solvated in the oxidized matrix, an additional oxidation and fluorination of the product took place, which led to a powerful loosening of the structure and obtaining of the result product of thinner dispersion. Further isolation of the product on dividing funnel allowed us to divide two phases formed during hydrolysis: hydrophilic (bottom, b) and hydrophobic (light, l).

RESULTS AND DISCUSSION

The composition of OG and FOG was calculated according to the results of element microanalysis for carbon and hydrogen, fluor was determined by alloying the sample with metallic sodium and further distillation and thymetric titration. Oxygen content was calculated from the difference between the initial weight and estimated weights of other components. Titration with a Br-selective electrode showed the presence of Br trace in the FOG compounds. An analysis of the data on OG element composition, presented in Table 1, showed that the increase in the oxidizer quantity in the reactive system up to 10g KMnO_4 did not lead to a variation in the product composition, which was defined as a preoxidized matrix state - graphite hydroxhydrate.

TABLE 1

Chemical composition oxides graphite obtained

N	OG	KMnO_4, g	Content, mass%*			C/O**	Calculated composition
			C	H	O		
1		0.5	86,43	1,1	8,47		
2		1,0	86,71	1,0	8 29		
3		3,0	86,56	1,0	8,44		$\text{C}_{14}\text{H}_2\text{O}$
4		5,0	86,56	1,0	8,44		
5		10	86,45	0,9	8,65		
6		15	79,85	0,9	15,25	6,96	$\text{C}_8\text{O}_{1,15}\text{H}_{1,08}$
7		25	78,75	0,8	16,45	6,30	$\text{C}_8\text{O}_{1,25}\text{H}_{0,98}$
8		35	73,60	0,9	21,50	4,57	$\text{C}_8\text{O}_{1,75}\text{H}_{1,17}$
9		50	69,67	0,8	25,53	3,64	$\text{C}_8\text{O}_{2,20}\text{H}_{1,10}$
10		65	66,26	0,9	28,84	3,07	$\text{C}_8\text{O}_{2,61}\text{H}_{1,30}$
11		80	57,53	1,0	37,47	2,04	$\text{C}_8\text{O}_{3,91}\text{H}_{1,50}$
12		100	57,23	1,0	37,77	2,01	$\text{C}_8\text{O}_{3,96}\text{H}_{1,51}$

* ashens remains 4 mass% was taken into account in calculations;
 ** a real C/O ratio was slightly higher because it was difficult to evaluate oxygen H_2O contribution correctly

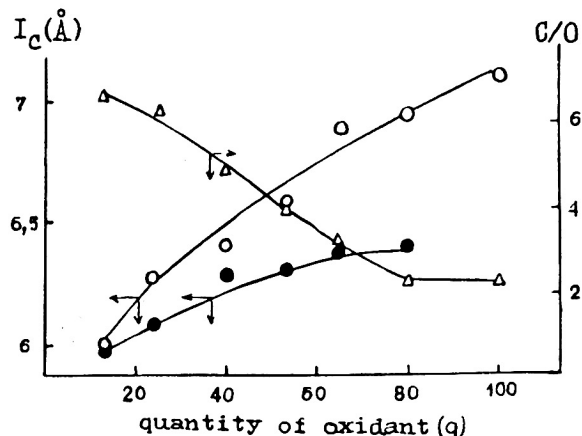


Fig.1. Variation of the C/O ratio (Δ) and correlation of identity periods of bottom (O) and light (\bullet) FOG phases with oxidant quantity in the system

TABLE 2
Chemical composition fluoroxides
graphite obtained

FOG	N Phase	Fluorine, Calculated mass%	Composition
1	l	33,60	$C_8F_{3,8}$
6	l	32,88	$C_8O_{0,95}F_{3,75}$
	b	31,38	$C_8O_{0,96}F_{3,60}$
7	l	34,37	$C_8O_{1,03}F_{3,73}$
	b	33,25	$C_8O_{0,99}F_{3,50}$
8	l	37,55	$C_8O_{1,26}F_{3,14}$
	b	31,76	$C_8O_{1,40}F_{3,10}$
9	l	33,14	$C_8O_{1,80}F_{3,30}$
	b	25,12	$C_8O_{1,90}F_{2,60}$
10	l	30,76	$C_8O_{2,20}F_{3,00}$
	b	24,12	$C_8O_{2,20}F_{2,40}$
11	l	24,00	$C_8O_{2,80}F_{2,60}$
	b	17,20	$C_8O_{4,60}F_{2,00}$
12	b	17,20	$C_8O_{4,60}F_{2,00}$

l - light phase; b - bottom phase

Beginning from OG-6, oxygen quantity in compounds increases passing through the maximum value in OG-11 (fig.1). Fluorination of OG with different degrees of oxidation leads to the formation FOG's fluorine content in which is presented in the tabl.2. The samples OG-1 - OG-5 are identical in their chemical composition, therefore, only OG-1 was subjected to fluorination. Fluorination degree of oxographite matrix decreases at the increase of oxidation degree of initial OG. Fluorine content according to results of chemical analysis attains its minimum value in FOG-11 and does not change after it (fig.2), testifying the

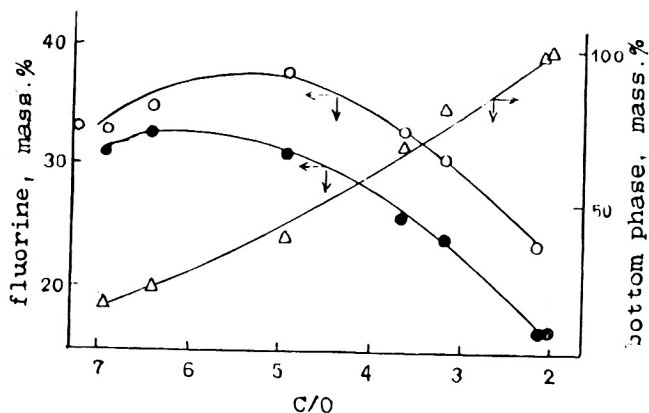


Fig.2. Variation of fluorine content in bottom (●) and light (○) FOG phases and mass% correlation of FOG phases (Δ) with initial OG degree of oxydation

absence of vacancies for further fluorination of carbon. According to the tabl.2 all FOGs but the last one divided into two pheses after hydrolysis different in hydrophilic properties. Beginning from FOG-7 a notable difference in fluorine content in light and bottom phases was observed that characterizes a different degree of fluorination of oxographite matrix fragments. It was determined that the weighting ratio of bottom and upper phases changes in such a way that all FOG-1 came to the surface, then the portion of bottom phase increased up to FOG-11, which precipitated almost utterly (fig.2).

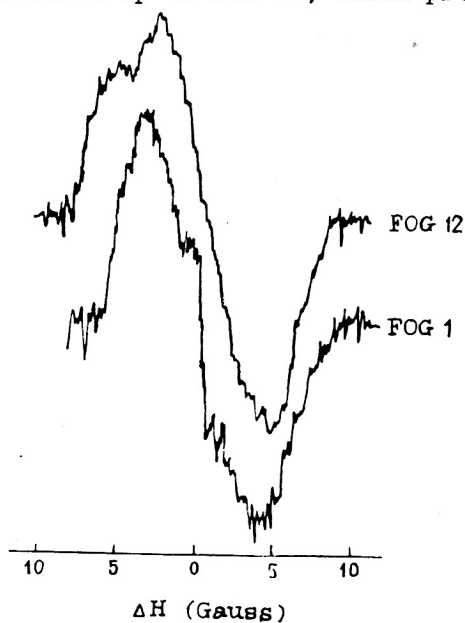


Fig.3. Differential ^{19}F NMR absorption spectra FOG-1 and FOG-12

IR- spectra of OG with high degree of oxidation revealed absorption in the range of 1070cm^{-1} (hydroxyl), 1720cm^{-1} (carbonyl) and 1600 and 3200cm^{-1} (absorbed water). IR-spectra of FOG's were identical on set of absorption lines differing by presence or absence of 1720cm^{-1} peak, typical for initial OG. In these spectra an intensive 1120cm^{-1} peak was present, which corresponded to peripheral CF_2^- and CF_3^- groups [3]. Besides a weak peak was observed at 1240cm^{-1} which was assigned to the C-F vibration of tertiary carbon atoms [1]. In contrast to the data published in [2] the absorption intensity in the 1240cm^{-1} range for all FOGs studied during this work was considerably lower. It could be due to a powerful destruction of the product structure during hydrolysis and, consequentely, by increase of the content of peripheral CF_2^- and CF_3^- groups.

The ^{19}F resonance were observed in the field of 2114 G in the interval temperatures 170-290K. ^{19}F NMR FOG-1 spectrum (fig.3) consist of 2 components - broad and narrow with chemical shift (CS) (centre of spectrum gravity) $560 \pm 15\text{ppm}$, which is situated in value area of fluorine CS in fluorographites with aromatic structure of carbon [4]. Presence of 2 lines in spectrum in a broad temperature interval allows to assume the existence of two unequivalent nuclei of fluorine, one of which (narrow) is weakly connected with carbon atoms and possesses some mobility in the crystal deficiencies or grain boundaries [5], these fluorine atoms have relatively large mobility. Although line shape of FOG-1 spectrum is analogous for one for C_2F [6], values of the second moments (S_2) of these compounds are considerably different, they are 5,3 and $10,2\text{G}^2$ respectively, it proves increase of distance between fluorine nuclei in the first compound. In this case S_2 is conditioned by dipole-dipole interaction of fluorine atoms. Therefore if to know this value, it is possible to evaluate medium distance between resonancing nuclei according to Van-Fleck formula; the distance is $1,98 \pm 0,1\text{A}$. ^{19}F NMR FOG-12 spectrum has an asymmetrical form (fig.3) and can be presented by superposition of 2 lines with CS ~ 560 and ~ 480 ppm. The latter value is typical for CS of graphite monofluoride (~ 470 ppm), which has alyphatic fragments in structure of the compound. It is impossible to evaluate correctly medium distance between fluorine atoms in FOG-12 even if to know S_2 value of NMR spectrum (4.1G^2) because of a strong mutual covering of spectrum constitutives.

Analysis of DTA curves of OGs row shows that beginning from OG-6 the exoeffect in the range of 210°C exists connected with destruction of oxygen-containing fragments of matrix. Oxygen from matrix appears in OG-6 in small quantity and increases at decrease of C/O ratio. On DTA FOG-1 curve exoeffect with maximum at 500°C is present. This exoeffect is connected with thermodestruction of structure and CF_4 isolation. Decrease of T_{exof} on $70-100^\circ\text{C}$ in comparison with data [7] can be explained by destruction of structural homogeneity of carbon net connected with method of FOG obtaining. Beginning from FOG-6 on DTA curves exoeffect in the range of 210°C appears and grows that corresponds to the initial OG-6. A peak corresponded to destruction of C-F fragments of the structure widens in the range of $330-510^\circ\text{C}$ and its maximum is displaced to the side of lower temperatures.

X-ray diffraction patterns of OG row shows, that redistribution of peak intensities corresponds to variation of phase ratio of graphite and OG in oxidation products. In diffractograms of the first 5 OG patterns near 2θ a very intensive peak (002) with $d=3,47\text{A}$ is present, characterizing identity period (I_c) in graphite hydroxohydrate. Beginning from OG-6 peak near $12^\circ 2\theta$ appears and grows, so in OG-11 a solitary signal with $I_c=7,1\text{A}$ is present (fig.4,a). FOG's X-ray diffraction shows broad intensive signal in $12-15^\circ 2\theta$ area (fig.4,b), widened at decrease of C/O ratio in the initial oxide. In the result of FOGs division on their hydrophilic properties we managed to find that they differed in I_c value (fig.2; fig.4 ,c,d). Maximum difference was observed for FOGs obtained on maximum oxidized matrix.

ESCA spectra of C1s-, O1s-, F1s-, Br3d-electrons were obtained with application of $\text{Mg K}\alpha$ -radiation. Resolution at $\text{Au } 4f_{7/2}$ was

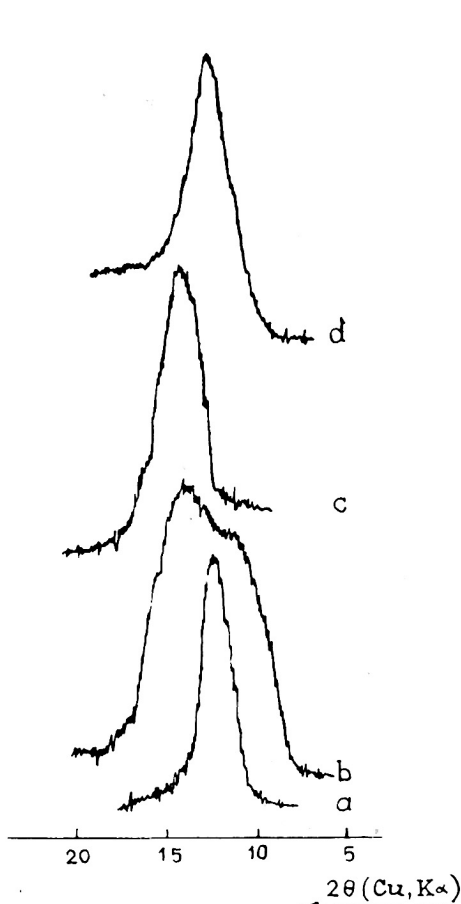


Fig.4. X-ray diffraction patterns:

- a - OG-11;
- b - unisolated FOG-11;
- c - FOG-11,1;
- d - FOG-11,b

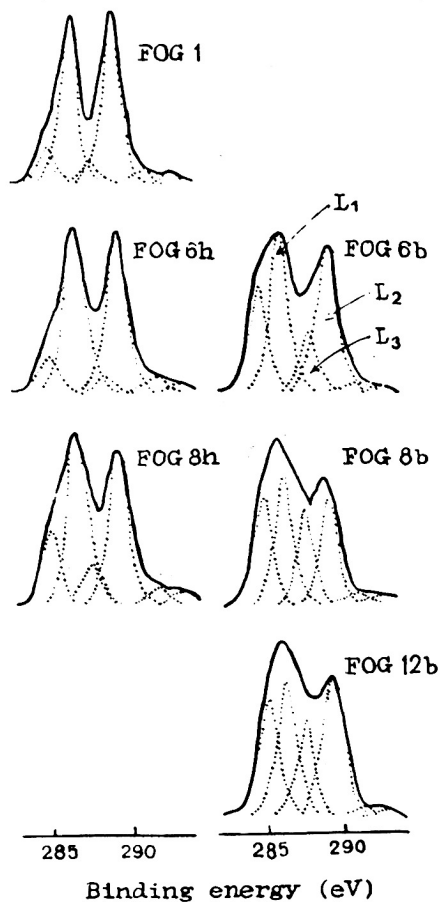


Fig.5. C1s spectra of FOG's isolated phases

1,5eV. Calibration of energy scale of the spectrometer was conducted according to the peak of hydrocarbon contaminations (285,0eV). Three main peaks may be marked in the ESCA spectra of C1s (L1,L2,L3). (fig.5). Binding energies (E_B) of L1 and L2 peaks for the samples in the beginning of the row lied in the ranges of (286,6±0,2)eV and (288,0±0,1)eV respectively and decreased at the end of the row to (286,2±0,2) eV and (287,4±0,2) eV. E_B of L3 peak lied in the range of (289,1±0,2)eV for all studied compounds. L1 peak could correspond to C-C bond. Integral intensities ratio of L2 and L3 peaks was accompanied by variation of O/F ratio. It's necessary to note that E_B of L3 were lower in comparison with these observed usually for covalent compounds like of $(CF)_n$ [7]. E_B of F1s band

maximum in the compounds lied in the range of $(687,5 \pm 0,2)$ eV and therefore interaction between carbon and fluorine has an intermediate character between typical covalent bond in compounds $(CF_2)_n$ and in ionic salt LiF. Additional peaks of C1s-spectra with high E_B and low intensity can correspond to carbon covalent bonded with one or more fluorine. Existence these peaks points at possible presence of alyphatic fragments on the surface of samples.

In the result of study of graphite oxidation process it is determined that a notable formation of covalent bond of oxygen with graphite matrix begins from ratio of graphite:oxidizer as 2:1. Further increasing of oxidizer concentration leads to an even increase of oxidation degree of graphite matrix up to C/O=2,1 at components ratio 1:3 respectively. Fluorination of a row of OG with different oxidation degrees showed that maximum fluorine content (37,5 mass.%) had been determined in the samples oxidized at ratio of graphite:oxidizer as 1:2,3. The existence of two different phases in FOG's row allows to assume that two interdependent phases are also present in the initial OG. Probably, oxidation begins from particle surface with maintenance of graphite structure in the basic volume; at further oxidation its portion decreases that leads to formation of homogeneous covalent bonds of carbon structures in highly oxidized OG. An obvious FOG division at increase of oxidation degree of the initial matrix reveals structural inhomogeneity in OG, characterizing ratio of graphite and oxographite structures. Therefore, the absence of bottom phase in FOG-1 and light one in FOG-12 is quite regular. According to experimental data bottom phase contains more quantity of carbonyl in comparison with light phase and their quantity grows at increase of oxidation degree of the initial OG, consequently, it is a fluorination product of just oxographite part of the matrix. It is evidently why structural parameters of bottom phase approach ones in OG-12 ($I_c=7,1\text{\AA}$).

Fluorination of oxographite matrix by the method described does not touch carbonyl fragments of the structure that is confirmed exoeffect calculation on DTA curves. Therefore, capability for formation of C-F bond in FOGs decreases at decrease of C/O ratio and reaches minimum value (17 mass%) which characterizes maximum degree of fluorination of the highest OG. Results of spectroscopic studies of FOG obtained showed presence of alyphatic fragments of the structure side by side with remains of two-measured carbon net, that could be explained if to take into consideration application of chemical dispersion in the process of obtaining of FOG's described.

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