Fluorination of lyophilized graphene oxide and graphene oxide-C60. Fluorination of graphite, graphite oxide and subsequent reaction of the prepared products.

Science

KEYWORDS : Graphite, graphene, fullerene C60, graphene oxide, lyophilization, fluorination, chlorination, hydrogen graphite, graphane, fluoride graphite

Eva Zemanová	State Office for Nuclear Safety, Senovážné náměstí 9, Prague 1, Czech Republic
Karel Klouda	VŠB Technical University of Ostrava, Faculty of Safety Engineering, Lumírova 13/630, Ostrava, Czech Republic
Eliška Brabencová	The State Institute of Nuclear, Chemical and Biological Protection, Kamenná 71, Czech Republic
Stanislav Brádka	The State Institute of Nuclear, Chemical and Biological Protection, Kamenná 71, Czech Republic
Karel Lach	The Institute of Public Health in Ostrava, Partyzánské nám. 7, Czech Republic

ABSTRACT

Oxidization of graphene and joint oxidization of graphene and fullerene C60 in various weight ratios were used to produce water suspensions that allow preparation of foils with various morphologies which can be further treated, e.g. by fluorination, bromination, embedding of catalytic-active metals, preparation of composite materials with other polymers or nanofibers and also as lamellar fibers prepared by freeze drying without any additional components.

In this work we have focused on fluorination of water suspensions of graphene oxide and graphene oxide–fullerene C60 after their lyophilization. The resulting products were characterized with microscopic imaging techniques, SEM, FT IR, EDAX elemental analysis, TGA and DSC analyses. The paper also revives author´s results which date back to 1985 when he dealt with fluorination of graphite and graphite oxide with elemental fluorine and subsequent processing of fluorination products. The obtained products, then called by the author hydrogen graphites, fluoride graphite and chloride graphite, are now known under as graphane, fluorographene and chlorographene respectively. This work deals with preparation of materials with amphiphobic properties, based on graphene oxide – fluorine and graphene oxide – C60 – fluorine.

Introduction

Our previously published works [1,2] describe methods of oxidization of fullerene C_{60}, graphite and a mixture of graphite and fullerene C_{60} in various weight ratios and identification of the prepared products with a focus on their functional groups, structure and thermal stability with FT IR, DSC, TGA, XRD and mass spectroscopy. In our work [3] we published results of bromination of such prepared graphite fullerene foils with liquid bromine and results of bromination of the graphene-oxide foil by reaction with bromofullerene. Another work [4] to be published soon describes properties of products obtained from matrices GO and GO-C60 prepared by lyophilization and their converted (reduced) forms. This work presents results of fluorination of lyophilized products of joint oxidization of graphite and fullerene C_{60}.

This work also uses old results from the author´s dissertation completed in 1980s [5] which contained several chapters on fluorination of graphite and graphite oxide with elemental fluorine, with subsequent processing of the fluorination products (repeated fluorination of the reduced products). In the then Czechoslovak Socialist Republic the possibility to publish results was very limited. In the work that followed [6] the author called the prepared product "hydrogengraphite" and now it is called *graphane.* Hydrogen attached to the C-skeleton of such products can be replaced with chlorine or fluorine under reaction conditions in which graphite does not react. In his earlier work the author called the product of fluorination "fluorographite" and now it is called *fluorographene.*

In essence, two possible methods have been described to prepare materials based on graphene–oxide and fluorine: the reaction of graphene–oxide (GO) with fluorination agents and oxidization of fluoride graphite. The fluorination of graphene-oxide can be performed with HF in water suspension [7]. The ratio C/F was in the range of 9.5 – 2.1, depending on the reaction time, temperature and the mutual ratio of GO and HF. Another fluorination agent is BF_3 – etherate in presence of alkylamine or alkylthiol, which facilitate release of the F ion for the reaction [8]. GO in water suspension was partly fluorinated by contact with HPF_6 at an increased temperature up to 160^0 C. The content of fluorine in the product was 3.2 – 4.3 wt. % [9]. Fluorination with the so-called modern fluorination agent DAST (diethylamino sulfur trifluoride), which is used for deoxofluorination of alcohols, aldehydes and ketones [10], resulted in reduction, i.e. the ratio C/O increased but the content of fluorine in the obtained product was 3-4 wt. %. The work [11] describes effects of a solvent on the increased content of fluorine in fluorination products of GO prepared with the fluorination agent DAST. Authors of the work [12] anticipate fluorination only on GO carbonyls to CF_2 and carboxyls to COF. In case of the DAST agent and the electron–rich substitutes on GO one may speculate about partial expansion of carbon circles [10]. The highest content of fluorine and carbon, up to 1:1, was achieved by direct fluorination employing honeycomb G-O with a large surface area and elemental fluorine in the temperature range 25-180^0C. [13]. C_2F exfoliated by sonification in the environment of N-methyl-2-pyreolidone was hydrolyzed at 170 C^0 with alkali hydroxide and subsequently oxidized. Its C-skeleton split to produce graphene fluoroxide, partially soluble in water [14].

Another method to prepare products with amphiphobic properties is oxidization of graphite fluoride $CF_{0,25,}$ e.g. with a mixture of sulfuric acid, trihydrogen-phosphoric acid and potassium permanganate [15] or joint pyrolysis of C_2F and graphene oxide at temperatures 500-800 C^0 in argon atmosphere [16]. A product of fluorination containing no oxygen (fluorographene) can be obtained by direct fluorination of graphene [17] with dissolved fluorine [18] or by mechanical or chemical exfoliation of graphite fluoride [19, 20]. Graphene can be retrieved from graphite fluoride by long-term sonification of $CF_{0.25}$ with sulfonate at 80^0C and subsequent reaction with KI at 240^0C [21]. Fluorination of fullerene C_{60} alone with elemental fluorine produced a wide range of products with various degrees of fluorination of the carbon molecule, with the general formula C_{60} F_{2K} K = 1-30. The fractions are differentiated based on the quantity of fluorine, e.g. C_{60} F_{30} - C_{60} F_{47} [22].

Experimental part

The employed chemicals and instruments

Graphite: PM – very fine crystalline powder graphite, mesh 0.025mm, Supplier: Koh-I-Noor Netolice, Czech Republic
Fullerene C_{60}: 99.5% purity, SES Research, Houston USA

ATR analysis by means of FTIR spectrometry was performed using the spectrometer Brucker Alpha/FT-IR, ART crystal (identified as Platinum Diamond 1 Ref1), software OPUS 6,5, source IR SiC Globar. Number of spectrum scans 24, resolution 4 cm^{-1}, spectrum range 375-4000 cm^{-1}.

Thermal analyses TGA and DSC of the prepared product were performed on STA 1500, Instrument Specialists Incorporated-THASS, analytical scale SUMMIT, SI 234-4, at flow rate 20 ml/min., heating rate 10°C/min., ceramic crucible, diameter 5 mm and height 8 mm, degradation medium air.

SEM Phenom FEI and SEM FEI Quanta 650 FEG (USA) were used for slides of products

Lyophilizer Free Zone 1L Benchtop, made by Labconco, model 7740030

Energy dispersion elemental X analysis EDAX, team EDS

NMR analysis: Varian XL – 100-15, chemical shifts ppm, ^{19}F are detected in respect to $CFCl_3$ [5]

Powder X-ray diffraction analysis: Mikromat Chirana Co/Fe [5]

UV lamp Tesla RVK: 125 W, used for chlorination in a silica reactor, joint aluminum case [5]

Determination of specific weight of the samples was performed by pycnometry at 20°C in n-butanol [5].

IR spectrometry Figs. 6 and 8: Perkin Elmer 2225, KBr Tablet, CCl_4, CS_2, Nujol suspension, FMIR [5]

DTA Figs. 4, 7, 9: Derivatograph 1500, M.O.M, Budapest [5]

2. Oxidization of fullerene C_{60}, graphite and a mixture of graphite-fullerene C_{60}

A detailed method of oxidization of fullerene C_{60}, graphite and a mixture of graphite-fullerene C_{60}, formation of water suspensions and preparation of foils were described in our previous publications [1, 2]. The weight ratios and representation of the individual components used for the oxidization are provided in Table 1.

Table 1. Weight representation of the individual components used for the oxidization

Ratio /weight (g)		$NaNO_3$ (g)	$KMnO_4$ (g)	H_2SO_4 (ml)	Product No.
graphite	C_{60}				
-	1/(0,7)	1	2	18	I. $C_{60\text{-oxi}}$
1/(1.5)	-	2	4,5	31	II. GO
1/(1.1)	1/(1.1)	3	7	52	III. GO-C_{60}
2/(1.5)	1/(0.7)	3	7	52	IV. GO-C_{60}
3/(1.75)	1/(0.55)	3	7	52	V. GO-C_{60}

Lyophilization

Lyophilization of water suspensions of the oxidized products of GO and GO–C_{60} was performed by means of a modified procedure described in a Czech patent [23]. The possibility to use this method for fiber formation (change of morphology) was tested for products GO (No. II) and GO-C_{60} (No. V) by means of controlled freeze drying (vacuum sublimation) from their water dispersion. Lyophilization of water suspensions was performed at -40°C, 0.153 mbar, for 18 hours , both for the oxidized and reduced forms.

Fluorination of lyophilized products No. II and No. V

Samples of products No. II (GO) and No. V (GO-C_{60}, 3:1) after the completed lyophilization were fluorinated. Fluorination was performed using a stationary method with 20% elemental fluorine at 2 bars at the room temperature for 21 hours. The elemental composition was determined by the EDAX method.

Fluorination of graphite and graphite oxide and subsequent reactions of the prepared products

Fluorographite (graphite fluoride) was prepared by direct fluorination of graphite with gaseous fluorine containing 6-8% HF in a continuous Monel reactor. The temperature during the fluorination ranged in the interval 450-500° C, fluorine was dissolved with nitrogen to the concentration of 20%. The o resulting fluorographites (graphite fluorides) were used as input products for further reactions indicated in Table 2.

Table 2. Fluorination of graphite and graphite oxide and subsequent reaction of the prepared products

Input reactants	Reaction conditions	Product
Graphite + F_2 (20%)	450 – 480°C, 12-18 hours	$CF_{0,83-1,2}$ (I)
$C_6O_3H_{1,5}$ + F_2 (20%)	100-110°C, 6 hours	$C_6O_{2,5}H_2F_{2,8}$ (II)
CF_x (I) + $LiAlH_4$	30-60°C, 6 hours, THF, Et_2O,dioxan	$C_6H_{1,1-1,32}F_{0,06-0,15}$ (III)
CF_x(I) + RMgBr	30-60°C, 6 hours , THF,Et_2O	$C_6H_{1,0-4,5}F_{0,18-2,7}$ (IV)
$C_6O_3H_{1,5}$ + RMgBr	30-60°C, 6 hours ,THF, Et_2O	$C_6O_{0,5-1,8H1,56-2,22}$ (V)
$C_6H_{2,61}F_{0,18}$ (IV) + F_2 (20%)	100-110°C, 6 hours	$C_6F_{4,92}$; e.g. $CF_{0,82}$ (VI)
$C_6H_{2,61F0,18}$ (IV) + Cl_2	160-165°C, UV	$C_6H_{0’29}Cl_{0’69}F_{0,06}$ (VII)
$C_6F_{4,92}$ (VI) + KOH	KOH, t-BuOH	$C_6F_{0,2}(OH)_{1,1}$ (VIII)
$C_6O_{0,66}H_{1,7}$ (V) + F_2 (20%)	100-110°C, 6 hours d	$C_6O_{0,63}H_{0,55}F_{3,9}$ (IX)

X = 0,83-1,2
R = $-CH_3$, $-CH_2CH_3$, -isPr, -Bu, $-C_6H_5$

Results

Fluorination of the lyophilized products No. II and No. V

Results of the EDAX elemental analysis of fluorinated lyophilized samples:

No. II (GO): $C_{12.9}\ O_{4.6}\ F$.

No. V (GO-C_{60}, 3:1): $C_{7.5}\ O_{3.5}\ F$.

The content of fluorine related to carbon is practically two times higher in the GO-C_{60} product, which can be explained by the role of the fullerene molecule and its higher reactivity to radical reactions on the carbon skeleton C_{60} .

The FTIR method was used to demonstrate C-F bonds. The value of wave numbers of C-F bonds vibrations depends on many factors, e.g. the degree of C_{60} fluorination: lower values of wave numbers were measured for the fluorinated molecules, e.g. C_{60}

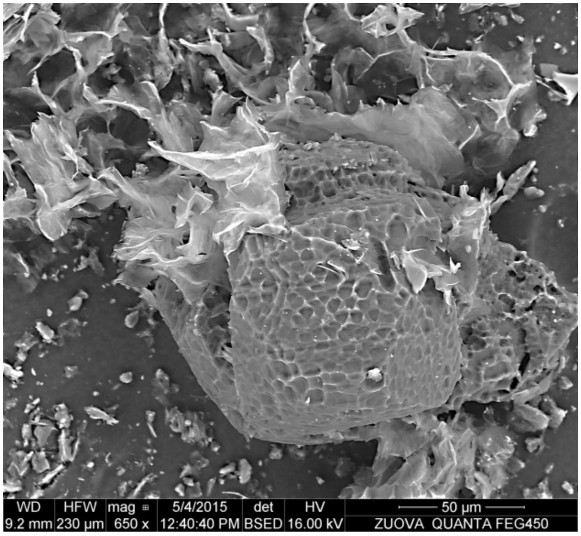
F_{30} (1125 cm^{-1}) and $C_{60}F_{47}$ (1240cm^{-1}). The values of wave numbers, and thus also the degree of covalence of the C-F bond, are affected by the bond curvature. The bond C-F (sp_3) vibrates at the wave number ca. 1082 cm^{-1}; for fullerene C60 at 1109-1136 cm^{-1}; the bond C-F on the surface S (W) CNT at 1123-1188cm^{-1} and for graphite fluoride at 1120cm^{-1} [24]. Another role is played by complex intramolecular interactions C-C, C-F, F-F, depending on whether the F atoms are in the same plane as the carbon skeleton. Strong peaks in the IR spectrum around 1000-1500 cm^{-1} demonstrate and identify the fluorinated circle, while peaks around 800cm^{-1} and 650 cm^{-1} are assigned to the swinging movement of the F-C-circle bond [25].

If we compare the measured IR spectrums (Fig. 1) of GO after fluorination and GO-C_{60} after fluorination there is a visible difference in the absorbance values and intensities of vibration peaks, mainly in the area 784-870cm^{-1}. Products of GO fluorination have the strongest vibration at the wave numbers 1018cm^{-1}, 1049cm^{-1} and 1083cm^{-1}. The product of GO-C_{60} fluorination demonstrates six equally intense vibration peaks in the range of 1122-785cm^{-1}. For this group we suppose that the vibration at 1122cm^{-1} corresponds to the C-F bond on the surface of a fullerene molecule. Vibrations at the wave numbers 1233-1230cm^{-1} can be found on both the fluorination products and the value is characteristic for the C-F bond perpendicular to the carbon skeleton (analogy of the C-F bond in graphite fluoride). The spectrums also contains peaks with high absorbance at 640cm^{-1} for $C_{12,9}O_{4,6}F$ and at 648cm^{-1} for $C_{7.5}O_{3.5}F$, which can be assigned to the swinging movement of the C-F bond. For both the fluorination products the IR spectrums contains a vibration characterizing a carbonyl group C=O, even though with a certain shift of the wave number from 1723cm^{-1} (initial GO) to 1743cm^{-1} (fluorinated GO) and from 1734cm^{-1} (initial GO-C_{60}) to 1744cm^{-1} (fluorinated GO=C_{60}), which may have lead to formation of groups –COF or –OF in the fluorination products . The shift of wave numbers was found also for the bond vibration of –C=C- , with a decrease in the intensity of absorbances from the category of very strong for the original products (before the fluorination) to weak (after the fluorination).

The scanning electron microscopy (SEM) has demonstrated different morphologies of the fluorinated products. The images show that surfaces of fluorination products of GO-C_{60} are more compact – see Figs. 2 and 3.

Fig 1. FT IR spectrumsoffluorinatedlyophilizatesa) No. II (GO); b) No. V (GO-C_{60},

a)



b)

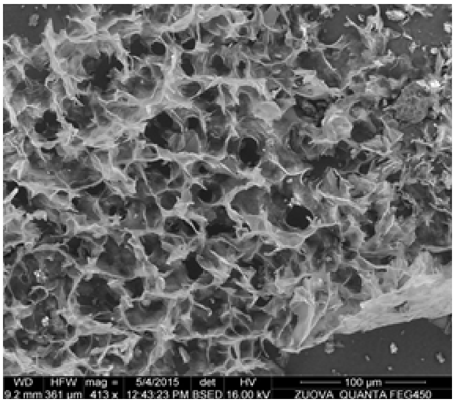
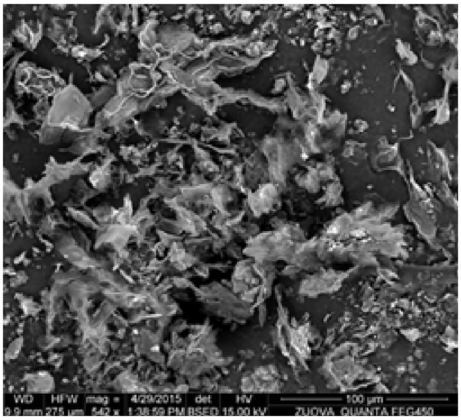


Fig. 2. Fluorinated lyophilizate of GO-C_{60}; 3:1 ($C_{7,5}O_{3,5}F$). a) line segment = 50µm; b) line segment = 100 µm

a)



b)

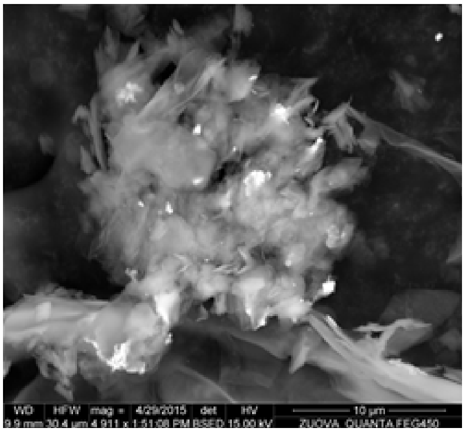


Fig. 3. Fluorinated lyophilizate of GO ($C_{12,9}O_{4,6}F$). a) line segment = 100 µm; b) line segment = 10 µm

Fluorination of graphite and graphite oxide and subsequent reaction of the products

Fluorination of graphite (I, Table 2) was used to prepare fluorographite $CF_{0.83-1.2}$ (*graphite fluoride – general formula* CF_x), where x depends on the time of fluorination. The value x affects the color of the product, from grey to snow white, and it also influences its thermal stability which increases with the growing value of x – see Fig. 4. In the IR spectrum the main valence vibration C – F keeps the wave number value of 1215 cm^{-1}.

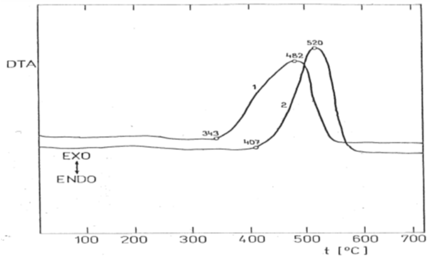


Fig. 4. Dependence of thermal decomposition of fluorographite CF$_x$ on the "x" value. [5]

Curve 1 – CF$_{0,83}$; curve 2- CF$_{1,2}$.

The fluorographite was reduced with LiAlH$_4$ (III, Table 2) and Grignard agent (IV, Table 2) to prepare hydrogengraphites. The new term for this product is graphane. These substances have hydrogen attached to the C-skeleton and it can be replaced with chlorine and fluorine under reaction conditions under which graphite does not react.

The reduction with LiAlH primarily demonstrated intercalation of the hydride: the space between the layers expanded from 585 pm to 824 pm. This expansion, along with nucleophilic attack of the hydride ion on the carbon atom, leads to polarization of the C-F bond and, finally, to release of fluoride ions and formation of LiF. The hydride anion is partly oxidized to a hydrogen atom by transfer of an electron to the C-skeleton and partly it is attached to carbon.

Fluorographite failed to produce Grignard agent, even after 14 days in contact with magnesium activated with up to 8% of iodine, both in ether and THF. Not even the dehalogenation occurred. There was a very intense reaction with alkylbromides to produce reduced products (IV, Table 2). It was not investigated whether the agent intercalated but, based on the released and identified olefins, the following prevailing reaction has been proposed:

C-F + H-CH$_2$-CH$_2$-MgBr C-H + CH$_2$ CH$_2$ + MgFBr

Fluorination of graphite at relatively high temperatures is accompanied by partial splitting of the graphite macromolecule to produce smaller polymer units, particularly CF$_x$, where x is greater than 1.1, which (after the reduction) enables partial solubility in THF, CHCl$_3$, CCl$_4$ etc. Thanks to the partial solubility it was possible to measure the 1H-NMR spectrum in CDCl$_3$ (Fig. 5) and IR spectrum in CCl$_4$ (Fig. 6) and thus to demonstrate covalent C-H bonds. With the increasing content of hydrogen the density of hydrogengraphites decreases (III-IV, Table 2) and it is practically half of that of the initial fluorographite: graphite 2.43 g/cm^3; CF$_{0.83}$ 2.73 g/cm^3; CF$_{1.1}$ 2.99 g/cm^3; C$_6$H$_{1.27}$ 1.96 g/cm^3; C$_6$H$_{2.6}$ 1.54 g/cm^3

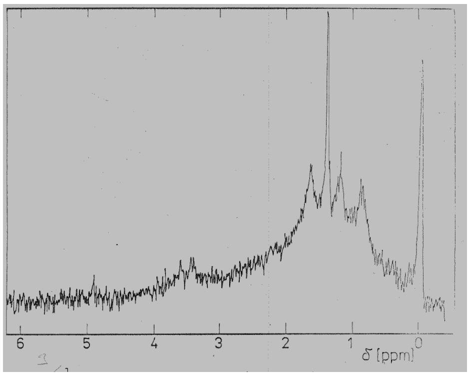


Fig. 5. ^{1}H - NMR spectrum of hydrogengraphite C$_6$H$_{3,2}$F$_{0,23}$ in CDCl$_3$ solution [5]

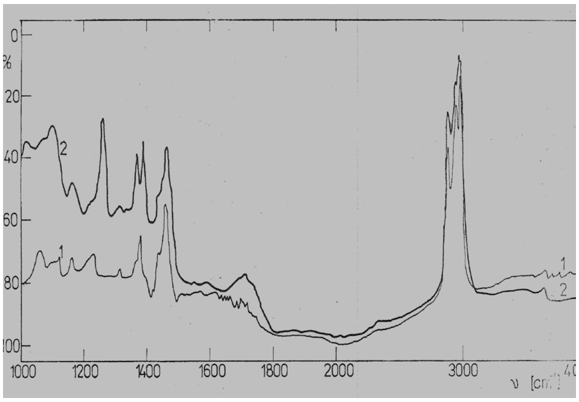


Fig. 6. IR spectrum of hydrogengraphite C$_6$H$_{3,2}$F$_{0,23}$ in CCl$_4$ solution [5]

Curve 1 - C$_6$H$_{3.64}$F$_{0.21}$; curve 2 - C$_6$H$_{3.2}$F$_{0.23}$

The powder X-ray diffraction analysis of hydrogengraphites has shown two to three diffusion lines hkl 100 220 pm, hkl 101 209 pm, hkl 110 122 pm. DTA was performed in the temperature interval 20-650^0 C. It has shown two exothermic effects for the sample C$_6$H$_{3.64}$F$_{0.22}$ with the maximums at 293^o C (beginning at 250^o C) and at 570^o C (beginning at 509^o C).

Fluorination of hydrogengraphite (newly called *graphane*) under the same reaction conditions as for the graphite, resulted in inflammation. The optimum temperature to prevent inflammation or rapid loss of weight (formation of volatile compounds of carbon and fluorine) was ca. 100^o C.

Powder X-ray diffraction analysis, DTA and IR methods were used to compare the prepared fluorographite (newly called *fluorographene*) CF$_{0.82}$ (VI, Table 2) with fluorographite of nearly the same elemental composition CF$_{0.83}$ (I, Table 2), prepared by fluorination of natural graphite at 450-480^o C.

The powder X-ray diffraction analysis of fluorographites:
CF$_{0.83}$ 585 (s) pm
CF$_{0.82}$ 217 (s) pm a 140 (vw) pm

DTA has shown relatively low thermal stability of the product CF$_{0.82}$ (VI, Table 2). The exothermic decomposition started as early as at 242 ^{0}C, which is by 100 ^{0}C lower than for fluorographite CF$_{0.83}$ (I, Table 2). Fluorographite CF$_{0.82}$ demonstrated two equal maximums at 310 ^{0}C and 374 ^{0}C, while for CF$_{0.83}$ the exothermic effect maximum was at 482 ^{0}C (Fig. 7).

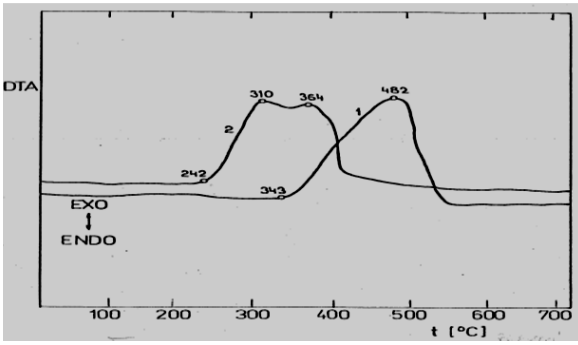


Fig. 7. Thermal decomposition of fluorographite.

Curve - CF$_{0.83}$ (I, Table 2); curve 2 - CF$_{0.82}$ (VI, Table 2) [5]

The IR spectrum of CF$_{0.82}$ manifested a major shift to lower wave numbers of valence vibrations of the C-F bond and instead of one intense band at 1215 cm^{-1} (Fig. 8) found for $CF_{0.83}$, there were three bands of approximately same intensities at 1176 (m), 1135 (m) and 1118 (s) cm^{-1}.

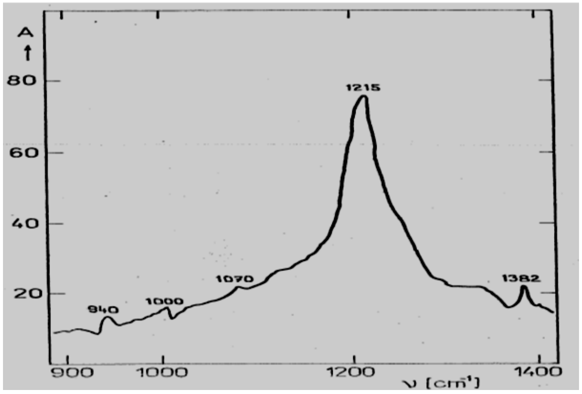


Fig. 8. IR spectrum of fluorographite $CF_{0.83-1.1}$ [5]

The new type of fluorographite (VI, Table 2) is disintegrated by dehalogenation equally as fluorographite (I, Table 2) in a reaction with KOH in a solvent but, differently from the latter, it is also partly subject to nucleophilic substitution on the C-skeleton which produces its hydroxy derivative $C_6F_{0.2}(OH)_{1.1}$ (VIII, Table 2). For this product IR spectroscopy has confirmed valence vibrations C-O (1024 cm-1, 1065 cm-1) and valence vibration O-H (3415 cm^{-1}). The thermal decomposition $C_6F_{0.2}(OH)_{1.1}$ (VIII , Table 2) occurs from 129 ^{0}C to 298 ^{0}C with a protracted exothermic effect associated with 23.6 % weight loss. This exothermic effect continually passes into the second one with the maximum at 385 ^{0}C (76.4 % weight loss). Hydroxygraphite $C_6F_{0.2}(OH)_{1.1}$ is slightly acidic, the measurement in the suspension water –acetone indicated pH = 5.6.The titration curve indicated the inflection point at pH = 8. The consumption in the inflection point was 38 mval per 100 g $C_6F_{0.2}(OH)_{1.1}$.

The chlorination of hydrogengraphite (IV, Table 2) initiated with UV was performed in the temperature range 47-210 °C. The highest content of chlorine in respect to carbon was achieved at temperatures160-165 °C, i.e. $C_{8.6}$ Cl and on the contrary, when the temperature was further increased to 200-210 °C the ratio declined to C_{15} Cl. The IR spectrum of the products of the chlorination (VII, Table 2) featured two absorbances with the maximums at 720 cm^{-1}(m) and 606 cm^{-1}(m) in an area characteristic for vibration of the bond C-Cl (760-538 cm^{-1}). The strongest absorbance in the measured range was found at 1005 cm^{-1} (vs), to which we assigned the vibration of C-C or C-skeleton. The thermal decomposition of the sample (VII, Table 2) occurred with two exothermic effects with the maximums at 274° C and 581° C; TGA and TG curves are shown in Fig. 9.

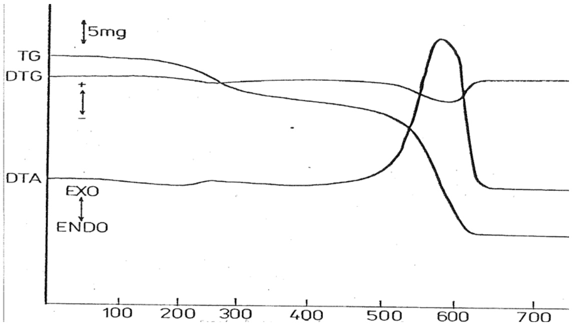


Fig. 9. Thermal analysis $C_6H_{0.29}Cl_{0.69}F_{0.06}$ (VII, Table 2). [5]

Also graphite oxide (newly called *graphene oxide*) is subject to partial reduction with alkylmagnesium bromide (V Fig. 1). The reduced product was fluorinated under the same experimental conditions as the products of fluorographite reduction (IV, Table 2). The resulting product had the summary formula $C_6O_{0.63},H_{0.55}F_{3.9}$ (IX, Table 2), where the ratio of C:F = 1:0.65. The content of oxygen essentially did not change after the fluorination and the resulting C-F bond was not subject to hydrolysis, as it was the case of the product II in Table 2, which had been prepared by fluorination of graphite oxide. This product II after 48 hours of hydrolysis demonstrated loss of fluorine up to 30 wt. %, which can be explained by hydrolysis of the bond –O-F or by washing of the sorpted HF.

IV Conclusion

The work presents old results from the author´s dissertation completed in 1980s which dealt with fluorination of graphite and graphite oxide with elemental fluorine and subsequent treatment of the products of fluorination by means of reduction, chlorination, nucleophilic substitution and repeated fluorination to prepare products called then by the author hydrogengraphites, fluorographites and chlorographites. At present, after the discovery of graphene, the same substances have been called graphane, fluorographene, chlorographene respectively and they have been reported under those names by the quoted authors and by many others. There are also some new results of fluorination of lyophilized products of joint oxidization of graphite and graphite - fullerene C_{60}.

Acknowledgment

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