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Fullerenec₆₀, Graphene-Oxide and Graphene-Oxide Foil with Fullerene and their Bromination

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Abstract- A direct reaction with liquid bromine was used to prepare bromo fullerene C_{60} Br₁₄₋₁₈. The brominated derivative reacted with previous lyprepared graphene-oxide (hereinafter GO), according to a method described by Hummer. The same method was used to oxidize graphite alone. The prepared graphite fullerene foil was brominated with liquid bromine and the graphene-oxide foil was reacted with bromo fullerene. FT-IR analysis of all the obtained products was performed and also TG Aanalysis to investigate particularly their thermal stability. The brominated products demonstrate lower thermal effects when thermally decomposed which is caused by the retarding ability of bromine.

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I. INTRODUCTION

raphite is an allotropic modification of carbon with sp2 bonds and made up of layers of A mutually interconnected hexagonal rings. The layers are arranged in parallel planes 335 pm apart. Carbon atoms in the adjoining layers are not chemically bonded to each other and they are attached by weak vander Waals forces that make it possible for various atoms or molecules in liquid or gaseous form to get in between the carbon layers. The resulting substances are called intercalation compounds of graphite and their characteristic parameter is the so-called "degree of intercalation", which indicates the number of carbon intercalated layers between two layers of an substance [1].

Depending on a type of the intercalated substance the graphite plane may be either an acceptor or donor of electrons. Another option is the so-called π -complex created by intercalation of substances of AXy type, where A is a metal or non-metal with a high valence status, X is an electronegative element and y is a stoichiometric coefficient.

Intercalates of graphite with alkali metals have been known since 1930s. They are called intercalates of the first degree with the formula C_8M (M=K, Rb, Cs), i.e.

they are characterized by a stacking sequence of layers of carbon and alkali metal.

Intercalates of graphite with alkali metals or in combination with other metals have been used in a number of applications as catalysts, e.g. for synthesis of ammonia, synthesis of carbohydrates by hydrogenation of carbon oxides, hydrogenation of olefins, they have sorption properties etc. [1]. Substituents can be chemically bonded to graphite under certain conditions by fluorination or oxidization.

Fluorination of graphite with elemental fluorine at 400-600°C produces a covalent compound called fluoro graphite CF_x , x = 0.25-1.12, depending on reaction conditions of the fluorination [1].

Oxidization of graphite with strong oxidizing agents (a combination of $KMnO_4$, $KCIO_4$, $NaNO_3$ and H_2SO_4) produces graphene oxide (GO), which is a precursor for chemical preparation of graphene [2].

GO is a compound made up of a carbon skeleton with main functional groups, such as carboxyl, carbonyl, epoxy and ether groups and hydroxy groups. These functional groups enable chemical reactions of GO [3] to form covalent bonds with other compounds (e.g. esterification, amidation).

Another option is a GO reaction to form noncovalent bonds [2]. The possible types of the bonds are hydrogen bonds, van der Waals forces, H- π , cation- π , anion- π , π - π , electrostatic forces. These non-covalent bonds are employed in preparation of composite polymers, biopolymers [4] and in use of adsorption and absorption properties of GO [5-7]. GO suspension can be vacuum filtered to prepare foils that find use in biology, electrical engineering, optics [8] and biomedicine [9].

Graphene can be prepared by a chemical method which consists in reduction of oxidized carbon (functional groups) in GO with various reducing agents (hydrazine, metal hydride, hydrogen, hydrogen iodide) or reducing methods, such as reflux in a polar solvent, microwaves irradiation, electrochemical reduction [12].

Another carbon modification from the nano particles group are fullerene sand their best known representative is fullerene C_{60} with a spherical molecule. Fullerene molecule may under gomostlynucleophilic and radical reactions [10].

Fullerenes are condensed polycyclic carbon substances with a cage structure and with even numbers of carbon atoms arranged preferably into

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pentagons or hexagons. The most perfect spherical shape has the fullerene C_{60} . Its surface is made up of twenty hexagons and twelve pentagons (similar to a classical sewn soccer ball). The pentagons are made of single covalent bonds and the hexagons are made up of a system of alternating single and double bonds.

The principal difference from graphite and diamond is the solubility of C_{60} in non-polar organic substances and its reactivity. Its typical reactions are associated with a transformation of arrangement from sp² to sp³ and thus with a reduction of tension in the molecule. The C_{60} molecule is electropositive which means that it prefers nucleophilic or radical addition on a multiple bond. Fullerene C_{60} can be used for hydrogenation, alkylation, halogenation, oxidation, polymerization etc.

The contribution describesour "combination experiment"

- Bromination of fullerene C_{60} + sub sequentreaction with GO
- Bromination of GO-C₆₀ foil and combination of GO with C₆₀

Functional groups of the resulting products were identified with FT-IR. We also determined their thermal stability which is the main topic of this contribution.

II. Experimental Part

Employed chemicals

Graphite PM – very fine crystalline powder graphite, mesh 0.025mm

Fullerene C $_{\rm 60},~99.5\%$ purity, SES Research, Houston USA.

Sulfuric acid, nitric acid, potassium permanganate, pyridine, tetrahydrofuran, liquid bromine, Supplier: Sigma – Aldrich.

Ultrasonification with PS 400A, power output 500 W, thermostat 75°C, frequency 35 Hz.

a) Measuring Instruments

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

Thermal analyses TGA and DSC of the prepared samples 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. Morphology of the products was determined with SEM Phenom FEI and SEM FEI Quanta 650 FEG (USA).

- b) Preparation of Graphene-Oxide (Hereinafter GO) by Oxidization of Graphite and Preparation of Graphene-Oxide- C_{60} (GO- C_{60}) by Oxidization of Graphite and C_{60} Mixture
- i. Sample weights for the individual experiments
- 1 g graphite, 0.5 g C₆₀, 2.11 g NaNO3, 4.6 g KMnO4, 35 ml H2SO4
- 2 g graphite, 2.8 g NaNO3, 6.5 g KMnO4, 45 ml H2SO4
- Graphite and mixtures of graphite + C₆₀ and GO+C60 were oxidized with a mixture of H₂SO₄, KMnO₄ and NaNO₃ according to Hummers and Offer man [11]. Graphite, sulfuric acid and sodiumnitrate (in the case of experiments I also fullereneC60) were placed into aflask, the mixture was stirred and cooled to10°C.

Potassium permanganate was subsequently added into the reaction mixture through a hopper in small doses. The mixture with the permanganate was slowly heated to 60°C and stirred at that temperature for 3 hours. Then it was left to stand for three days at the laboratory temperature.

The obtained products were filtered off, washed with a big quantity of distilled water until negative reaction to sulfate anions and dried for three days on a Petri dish at 50-60°C to form foils of GO and GO-C_{60} .

c) Bromination of Fullerene

FullereneC₆₀ (4 g) was added into liquid bromine 27.5 ml (85.3 g) and the mixture was agitated at the laboratory temperature for 72 hours. The excessive bromine was removed by drying at 75°C for 24 hours until constant weight. The yield was 9.9 g of greenbrown sub stance. According to the weight increase and subsequent telemental analysis, the average composition was $C_{60}Br_{14-18}$.

d) Modification of Graphene - Oxide (GO) by Reaction with Fullerene Bromo Derivative

GO (0.23 g) from the foil that was cut into tickets sized 2x5 mm was placed into THF (25 ml). The mixture was ultrasonificated for 10 minutes at the laboratory temperature to form suspension of GO in THF. Subsequently, we added fullerene bromo derivative (0.4 g) and 0.3 ml of pyridine. The suspension was brown. The reaction mixture was ultrasonificated for 10 minutes and then left for 24 hour sand intermittently stirred. The suspension was yellow-brown. The solid component was vacuumfiltered off and the filter cake was washed with 25 ml HCl (1:3) and 40 ml THF and subsequently dried at 50°Cfor 2 hours. The process produced 0.6 gof the product.

e) Bromination of $GO-C_{60}$ with Liquid Bromine

The GO-C $_{60}$ foil (0.15 g) was ultrasonificated in a flask in 10 ml of water solution and then liquidBr2 (4-5

ml) was added. There action mixture was left to stand for 15 day sat the laboratory temperature and intermittently stirred. The content of the flask was poured out on a Petri dish and gradually evaporated.



Fig. 1 : Gradual evaporation of brominated $GO-C_{60}$ at 35-45°C; reaction of $GO-C_{60}$ with Br Lin water environment

III. Results

a) Identification of Bromo fullerene

There is a number of publications relating to halogen derivatives of fullerenes [13-20] and describing preparation and identification of bromo and chloroderivatives of fullerenes C₆₀. The content of bromine in C_{60} Br_n is defined in the range2 < n < 24 depending on the reaction conditions (direct contact with bromine, reactionina solvent, reaction time and temperature, etc.), while the bromine content greater than n=24isascribed to an adduct with bromine; also adducts with a solvent have been described in those cases where the bromination is performed insolvents, e.g. in CS₂, CHBr₃, C₆H₄C₁₂ etc. In our case the bromo derivative of fullerene was prepared by direct contact with liquid bromine. The average composition of the product was determined by elemental analysis and by surface analysisasC₆₀ Br¹⁴⁻¹⁸.



a) C₆₀

100 pm

b) C₆₀ Br₁₄₋₁₈



Fig. 2: a) Electron image of fullerene, b) bromo fullerene c) Energy-dispersive X-ray Spectroscopy (EDAX)



Fig. 3: IR spectrum of the bromo derivative of fullerene

FT-IR spectrums were used to identify the following vibrations: 1242 w, 911 w, 844 vs, 773 vs, 749 m, 718 m, 543 m (cm-¹) - Fig. 3,the strongest of which is844 cm-¹ and it corresponds to the published data of the strongest vibrations for the bond C-Br. We have also provided the IR spectrum of the initial fullerene C_{60} for comparison (Fig. 4). $C_{60}Br_{24}851$ cm-¹ [14], $C_{60}Br_8849$ cm-¹ [14], C_{60} Br₈ 847 cm-¹ [15], $C_{60}Br_{24}849$ cm-¹ [15], $C_{60}Br_{14}842$ cm-¹ /[15], $C_{60}Br_{24} \circ 2xBr_2 846$ cm-¹ [16].





The following data were published on thermal stability of the prepared products of fullerene bromination:

 $C_{\rm 60} Br_{\rm 24^{-}}$ 2 levels of decompositionat 45°C and 170°C [16]

 $C_{60}Br_{24}\text{-}$ at100°C the beginning, the maximum at162°C [17-18]

C₆₀Br₂₄- at 90°C [14]

C60Br8- at 70°C-the beginning of decomposition [14]

The pressure of developed gasesre leased by decomposition of C_{60} Br₆ was measured [17] and based on the obtained values the authors assumed gradual decomposition with partial maximums at 138°C, 175°C and 204°C while in the temperature interval 90-187°C1 atom of bromine will bereleased from the cyclopentanecircle and cyclopentadienyl radical will operate as an inter media test age of the decomposition. Then 5 remaining atoms of bromine are expected to be released. The author santicipate a similar course of decomposition also for C_{60} Br₂₄.

For our C_{60} Br₁₄₋₁₈ the shape of the DSC curvesis different in the end other mic process area. In this area we anticipate release of bromine. For the bromo derivative alone the temperature range of the end other mic process is 62°C (126-188 °C) and the shape of the DSC curve is protracted(see Fig.No.5) which may hide partial maximum sand indicate a step-like release of bromine eviaintermediate products of decomposition, e.g. $C_{\rm 60}\,Br_{\rm 8}.$

The endothermic effect is 326.8 kJ/kg with the weight loss of 57%, the exothermic effect occurs in the temperature interval 418 – 504 with Δ H 4233 kJ/kg with the weight loss of 32%.A 10% weight loss of the sample occurred between the endothermic and exothermic processes (see Fig. 5).



Fig. 5 : Thermal analysis of the initial bromo derivative C_{60} Br₁₄₋₁₈ (degradation medium: air, air flow rate 20 ml/min, temperature 25-600° C, heating rate 10°/min, sample weight 9.3 mg)

In order to confirm the main source of the weight loss during the end other mic process we heated the sample to 250°C and analyzedit with FT-IR spectroscopy. The obtained spectrumin Fig. 6 corresponds to the IR spectrum of the initial fullerene (compare Figures 4 and 6). This confirms our assumption that all bromine is released up to the temperature of 250°C.



Fig. 6 : IR spectrum of fullerene bromo-derivative after heating to 250° C

b) Modification of Graphene-Oxide by Reaction with Fullerene Bromo Derivative

The measured spectrum of the obtained product is shown in Fig. 7. Spectrums of the initial substances are provided in Fig. 8 and Fig. 3 for comparison.



Fig. 7 : IR spectrum of a product of the reaction of GO with fullerene bromo derivative

Dominant vibrations:

For GO the skeletonvibration is at 1613 cm⁻¹ and the vibration of C=C bonds in GO-C60Brisat 1610 cm⁻¹ and it is no more dominant.

There are new dominant vibration sat 1091 cm⁻¹ and 1045 cm⁻¹ that include bond vibrations of a whole range of possibilities from epoxides, hydroxyles, C_O_C (for GO the value was 1068 cm⁻¹).

A similar range of the potential groups for GO is covered by vibrations at 1068 cm-1 and 979 cm⁻¹.

Vibration scharacterizing the groups C=O for $GOC_{60}Brx$ shifted towards the higher value 1745 cm-1in comparison to 1727 cm-¹ for GO.



New vibrations characterizing C-Br bonds were measured as dominant for GO C_{60} Brxat741 cm-1and 672 cm-¹ (the value of 845 cm-¹ for C-Br in the initial bromoderivative, which was dominant in it, was also found for the same bond in GO C_{60} Brx with a lower absorbance value – 839 cm-¹). The broad absorbance band 2400-3500 cm-¹ was divided, which probably corresponds to the O-H valence vibration of new carboxyl functional groups. Newvibrations, which had not been identified for GO and bromo fullerene, appeared for the productat1534 cm-¹, 1478 cm-¹ and 1417 cm-¹.

c) Thermal Tests of the Products

Fig 9.Thermal analysis of a product of GO reaction with fullerene bromo derivative (degradation

medium: air, air flow rate 20ml/min, temperature 25-600°C, heating rate 10°/min, sample weight 8.6 mg).



Fig. 10 : Thermal analysis of GO foil (degradation medium: air, air flow rate 20 ml/mintemperature 25-600°C, heating rate 10°/min, sample weight 10.0 mg).

The comparison of thermal stabilities of the initial GO, the used fullerene bromo derivative and the prepared product has shown that the first exothermic process starts for GO at190.9°C with the maximum at 225°Cand with the thermal fect of 508.4 kJ/kg. For the prepared product the first exothermic process starts at atemperature by 40°Clower, with the maximum at 64°C and with a lower thermal effect, specifically 385.9kJ/kgsee Fig. 9,10andTab.1, 2). The thermal effect of the second exothermic process is also lower and it is approximately one half of that of GO. The weight loss during the first exothermic process of GO is more than 20% lower than that of the prepared product. In case of weight loss during the second process the situation is reverse. The total thermal effect of the decomposing reactionis significantly higher than in the case of theinitial GO. For the fullerene bromoderivative alone the decomposition (debromination) occurs in the temperature interval 124-184°C with an endothermic effect (161kJ/kg) and with a significant weight loss of 47.6%. This explains the lower thermal effect during the first exothermic process of the prepared product and the

higher weight loss than for GO alone. Further decomposition of the initial fullerene bromo derivative occurs in the temperature interval 459-569°C, which is ca. by 60°C higher than the temperature of the second exothermic process of the prepared product.

| Table | 1 : Division of the TGA curve into |
|-------|------------------------------------|
| | temperature intervals |

| SampleN | Thermal | Temperature | Weight |
|------------------------|------------|---------------|----------|
| 0. | processNo. | range (°C) | loss (%) |
| | 1 | 25.0 - 169.4 | 10.1 |
| | 2 | 169.4 – 178.0 | 66.3 |
| GO-C ₆₀ Brx | 3 | 178.0 – 268.3 | 5.1 |
| (x=14-18) | 4 | 268.3 - 362.0 | 13.0 |
| | 5 | 362.0 - 458.7 | 1.4 |
| | 6 | 458.7 - 600.0 | 3.8 |
| | 1 | 25.0 - 142.4 | 11.0 |
| | 2 | 142.4 – 213.5 | 8.8 |
| CO foil | 3 | 213.5 – 222.3 | 43.6 |
| | 4 | 222.3 - 368.8 | 2.8 |
| | 5 | 368.8 - 473.0 | 18.1 |
| | 6 | 473.0 - 600.0 | 6.1 |

| Table 2 : Parameters | of the ongoing thermal | processes | (DSC) |
|----------------------|------------------------|-----------|-------|
| | | 0.000000 | (|

| Sample No. | Thermal processNo. | Temperature range (°C) | ΔH (kJ/kg) * | H _{f1} (mW) | $\Sigma \Delta H$ (kJ/kg) |
|--------------------------|--------------------|---------------------------|----------------------|----------------------|---------------------------|
| | 1 | 25.0 – 126.5 | 517.1 | 8.2 | |
| $GO-C_{60}Brx (x=14-18)$ | 2 | 150.5 – 195.4 | -385.9 | 75.5 | -517.1 |
| | 3 | 366.9 - 465.8 | -648.9 | 22.5 | |
| | 1 | 25.0 – 154.1 | 874.6 | 15.8 | |
| GO foil | 2 | 190.9 – 241.1 | -508.4 | 107.4 | -910.6 |
| | 3 | 356.5 – 492.1 | -1277.1 | 31.0 | |

 $^{*}\Delta H = thermal effect of the process based on the DSC curves$

 $(\Delta H > 0...endothermic \ process, \Delta H < 0...exothermic \ process)$

Fig 11.Shows the complex surface structure of the prepared product $GO-C_{60}$ Brx (x=14-18).

- d) Reaction of $GO-C_{60}$ Foil with Liquid Bromine
- i. Evaluation of the IR Spectrum of GO-C₆₀ Foil Brominated with Liquid Bromine

The IR spectrums of GO-C_{60} and its brominated product (Fig. 12 and 13) demonstrate the following general differences: wave number shifts, changes in values of absorbances and changes in intensities of vibrations with common assignment for both the substances, such as e.g. changes of mutual intensities of vibrations of the -C=C- bond in respect to C-O-C (from 1:1 for GO-C₆₀ to 1:3 for [GO-C60] Brx), increase in vibration intensities of the bonds -C=O or -COOH compared to -C=C- (3x for [GO-C₆₀]-Brx).

The main shift in the vibrations occurred for the broad band characterizing bond vibrations of the -OH

group, where the maximum of absorbance for $GO-C_{60}$ is at the value lower by ca. 200 cm⁻¹. The vibration of the C-O-C group for $GO-C_{60}$ has the wave number higher by 24 cm⁻¹.

A significant difference of the IR spectrum of the brominated derivative is the presence of vibrations at 871 cm⁻¹ and 571 cm⁻¹, to which we have assigned the valence vibration of the C-Br bond, and the presence of a new strong vibration at 1153 cm⁻¹, which can be assigned both to the deformation vibration of the C-Br bond and to deformation of C-CO-C and valence of C-O. Another difference consists in the fact that the spectrum of the bromo-product practically lacks any absorbance in the interval 1220-1380 cm⁻¹, which had been present as medium strong in the spectrum of the initial GO-C₆₀ and which we had assigned to the epoxy groups, deformation of -OH and etheric groups.



Fig. 11 : Electron image of a product of GO reaction with $C_{60}Br_{14-18}$, different scales



Fig. 12: IR-spectrum of the initial GO-C₆₀



Fig. 13: IR-spectrum of [GO- C₆₀]-Brx

e) Thermal Stability of the GO-C₆₀ Foil Brominated with Liquid Bromine

For the brominated GO-C₆₀ product he thermal analysis has demonstrate done endothermic process and two exothermic processes(Fig. 14). Unlike the TGA analysis of the GO-C60 foil, the brominated product $C_{\rm 60} Br_{\rm 14\text{-}18}$,when thermally exposed, does not manifest such a sharp weight loss as the GO-C₆₀ foil. In the temperature interval 213 - 222°Cthe weight loss was 44% (Fig. 15) and forC60Br14-18in the temperature interval 126 – 188°Cthe weight loss was 56% (Fig.5).Therefore, with a certain approximation, we can assume a gradual loss of weight (Tab. 3).The endothermic process in the product brominated with liquid bromine comes earlier than in the case of C_{en}Br14-18andits thermal effect is ca. 4 times bigger. The second exothermic process starts at a higher temperature in comparison with GO-C₆₀, while the first exothermic process occurs at a lower temperature.

Also interesting is the overall result of the thermal processes in the course of thermal

decomposition, which is significantly smaller for brominatedGO-C60foil (301kJ/kg) than for the initial GO-C60foil (1204 kJ/kg). For C_{60} Br₁₄₋₁₈ it is up to 3906 kJ/kg. In this case an important role in the total thermal effect is probably played by the considerable size of the endothermic effect of the brominated foil.

Bromine water with oxidizing effects may cause an increase in the number of carbonylorcarboxyl groups, due to splitting of the C-O-C bond. This can be concluded from the IR spectrum (absence of vibration sin the interval 1220-1380 cm⁻¹). Moreover, it is not possible to exclude addition of-OH Br+ on the moleculeor substitution of H+ with bromine in the carboxyl. Based on a comparison with the size of the endothermic effect in $C_{60}Br_{14-18}$ we anticipate various types of bromine bonds to the molecule. The size of the endothermic effect may also result in formation of anadduct of bromine and the molecule.



Fig. 14: Thermal analysis [GO- C₆₀]-Br (degradation medium: air, air flow rate 20 ml/min, temperature 25-600°C, heating rate 10°/min, sample weight 10.05 mg)



Fig. 15 : Thermal analysis foil GO-C₆₀ (degradation medium: air, air flow rate 20ml/min, temperature 25-600°C, heating rate 10°/min, sample weight 10.0mg)

| SamploNo | Interval | Temperature | Weight loss |
|-------------------------|----------|---------------|-------------|
| Sampleno. | No. | range (°C) | (%) |
| | 1 | 25.0 - 56.7 | 2.7 |
| | 2 | 56.7 - 114.0 | 20.3 |
| | 3 | 114.0 – 165.1 | 20.3 |
| | 4 | 165.1 – 259.4 | 12.6 |
| GO-С ₆₀ -Ы | 5 | 259.4 - 313.1 | 14.8 |
| | 6 | 313.1 – 504.1 | 12.6 |
| | 7 | 504.1 - 546.6 | 14.3 |
| | 8 | 546.6 - 600.0 | 0.9 |
| | 1 | 25.0 - 87.1 | 4.4 |
| | 2 | 87.1 – 153.0 | 8.2 |
| CO C foil | 3 | 153.0 – 197.0 | 8.0 |
| GO-C ₆₀ IOII | 4 | 197.0 – 205.0 | 51.1 |
| | 5 | 205.0 - 281.3 | 10.8 |
| | 6 | 281.3 - 490.9 | 18.0 |

Table 3 : Division of the TGA curve into temperature intervals x

X the indicated intersections of tangents to the respective bends of the TGA curve

Table 4 : Parameters of the ongoing thermal processes (DSC)

| Sampl eNo. | Thermal effect No. | Temperatur e range(°C) | ∆H (kJ/kg) * | H _{f1} (mW) | ΣΔH (kj/kg) |
|---|--------------------------|---------------------------|--------------------|-------------------------|-----------------|
| GO- C ₆₀ -Br GO- C ₆₀ foil | 1 | 25.0 – 131.9 | 1288.6 | 32.0 | |
| | 2 | 131.9 – 171.9 | -180.1 | 21.8 | -301.3 |
| | 3 | 253.3 – 322.8 | 81.5 | 2.0 | |
| | 4 | 478.6 – 557.3 | -1490.7 | 67.2 | |
| | 1 | 42.0 – 124.2 | 141.7 | 6.4 | |
| | 2 | 182.6 – 221.5 | -308.7 | 71.1 | - 1204. 1 |
| | 3 | 319.7 – 481.6 | -1037.1 | 28.1 | |

 $\Delta H = thermal effect of the process based on DSC curves (\Delta H > 0...endothermic process, \Delta H < 0...exothermic process)$ H_{it} = height of the peak of a thermal process on the DSC curve in an absolute value related to the point corresponding to the beginning of the thermal process

IV. DISCUSSION

Tens and hundreds of products (substances) have been described which were prepared by functionalization of graphene or graphene-oxide while forming both covalent and non-covalent bonds [21]. These products have different physicochemical properties. In the case of grapheme the reactions proceed via areactiveinter mediate, such as radical, carbene, aryne, nitreneornewly bonded substances [22]. Functional groups, such as–OH, -COOH, epoxy are used for the reaction of graphene-oxide. A classical example is a reaction with amines [23] when the group – COOH converts into COCI and the latter reacts readily with an amino group of the new substituent.

Graphene-oxide can be also functionalized with non-covalent bonds (van der Waals forces, hydrogen bonds, π - π interaction). As an example, we can provide its reaction with polymers, surface active substances, biomolecules etc. [24].

In the case of grapheme and fullerene a product has been described with anointer connection basedon π - π interaction. The product has interesting thermoelectric properties [25]. The interconnection of fullerene and GO with a covalent bond has been also described, specifically there action of substituted fullerene (-OH, -NH₂), fullerene pyrolidine, 1, 2 methano-fullerene– 61 – carboxyl acid [26-28] with active GO groups.

V. Conclusion

A direct reaction with liquid bromine was used to prepare bromo fullerene $C_{60}Br_{14\cdot18}$. Further, grapheneoxide (GO) was prepared and reacted with the brominated fullerene. Results of the performed analyses have not positively shown whether the reaction of GO with $C_{60}Br_{14\cdot18}$ lead to functionalization of GO with covalentor non-covalent bonds. Weassume potential partialesterification, also thanks to the alkalineenvironment. The shape of the thermal curve of a product of GO reaction with $C_{60}Br_{14}\cdot18$ is similar to that of GO and GO- C_{60} .

Another alternative was direct bromination of a GO-C_{60} mixture or foil created from the product. It was accompanied by partial oxidization, i.e. oxidization splitting of C-O-C bonds, epoxide bonds and bromination. The thermal decomposition of the product proceeded without external weight losses (unlike in the case of GO and initial GO-C₆₀).

In the process of thermal decomposition the prepared brominated GO and GO-C_{60} demonstrated lower thermal effects, which was caused by retardantability of bromine.

References Références Referencias

- Klouda, K., 1985. Interkalární sloučeniny grafitu. (Intercalate compounds of graphite) Dissertation, VŠCHT Praha (available in the technical library in Prague 6 – Dejvice).
- Makharza, S., Cirillo, G., Bachmatiuk, A., Ibrahim, I., Ioannides, N., Trzebicka, B., Hampel, S., Rümmeli, M.H., 2013. Graphene oxide-based drug delivery vehicles: functionalization, characterization, and cytotoxicity evaluation. Journal of NanopartRes, 15, 2099.
- 3. Zhang, Y., Ren, L., Wang, S., Marathe, A., Chaudhuri, J. and Li, G., 2011. Functionalization of

graphene sheets through fullerene attachment. Journal of Materials Chemistry, 21, 5386.

- 4. Yoo, B.M., Shin, H.J., Yoon, H.W., Park, H.B., 2013. Graphene and graphene oxide and their uses in barrier polymers. Journal of Polymer Science: Polymer Physics.
- Kyzas, G. Z., Deliyanni, E. A. and Matis, K. A., 2014. Graphene oxide and its application as an adsorbent for waste water treatment. J. Chem. Technol. Biotechnol., 89, 196-205.
- 6. Fakhri, A., 2013. Adsorption characteristics of graphene oxide as a solid adsorbent for aniline removal from aqueous solutions: Kinetics, thermodynamics and mechanism studies. Journal of Saudi Chemical Society.
- Chabot, V., Higgins, D., Yu, A., Xiao, X., Chen, Z. and Zhang, J., 2014. A review of graphene and graphene oxide sponge: material synthesis and applications to energy and the environment. Energy Environ. Sci., 7, 1564-1596.
- Russo, P., Hu, A., Compagnini, G., 2013. Synthesis, Properties and Potential Applications of Porous Graphene: A Review. Nano-micro letters, 5(4), 260-273.
- Shen, H., Zhang, L., Liu, M., Zhang, Z., 2012. Biomedical Applications of Graphene. Theranostics, 2(3), 283-294.
- Troshin, P.A., Lyubovskaya, R.N., 2008. Organic chemistry of fullerenes: the major reactions, types of fullerenee derivatives and prospects for their practical use. Russian Chemical Reviews, 77(4), 305-349.
- 11. Hummers, W.S., Offeman, R.E., 1958. Preparation of Graphitic Oxide. J. Am. Chem. Soc., 80 (6), 1339.
- Dreyer, D.R., Park, S., Bielawski, Ch. W. and Ruoff, R.S., 2010. The chemistry of graphene oxide. Chemical Society Reviews, 19, 228-240.
- Peel, J.B., Roth well, 1994. C₆₀ Framework Response to Halogen Addition: The Stable Isomers of C₆₀Br_{2m}.Aust. J.Chem, 47, 131-141.
- 14. Resmi, M.R., Smitha, K., Pradeeo, T., 1997. Thermal Decomposition of $C_{60}Br_{24}$ and $C_{60}Br_8$: Absence of sequential elimination. Proc. Indian Acad Sci, 109, 221-228.
- 15. Troshin, P., A., Kemnitz, E., Troyanov, S., I., 2004. Characterization of reactions of fullerenee C60 with bromine. Crystal structures of bromofullerenees $C_{60}Br_{6}$, $C_{60}Br_{6}$. CS_2 , $C_{60}Br_8$.CHBr_3.2Br_2, and $C_{60}Br_{24}$. $C_6H_4Cl_2.Br_2$. Russ.chem.bull, Inter. ED, 53, 2787 – 2792.
- Troshin, P.,A., Kolesnikov, D., Burtsev, A.,V., Lubovskaya, R.,N., Denisenko, N.,I., Popov, A.,A., Troyanov, S., I., Boltalina, O., 2013. Bromination of 60 Fullerenee. High-Yielo Synthesi of C₆₀Brx, (x = 6, 8, 24). Fullerenes, Nanotubes and Carbon Nanostructures 111, 47-60.

- Gayathri, S.S., Kamruddin, M., Tyagi, A.,K., Patnaik, A., 2003. Establishing akinetic control regime for the decomposition of brominated fullerenee derivates: C₆₀Br₂₄ and C₆₀Br₆, Chem.Phys. Lett, 374, 33-40.
- 18. Troyanov, S., I., Shustova, N., B., Popov, A., A., Sidorov, L., N., 2005. Synthesis and structures of C_{60} fullerene chlorides. Russ. Chem. Bull. Inter.ED, 54, 1656 1666.
- Troshin, P., A., Lyubovskaya, R., N., Ioffe, I., N., Shustova, N., B., Kemnitz, E., Troyanov, S., I., 2005. Synthesis and Structure of the Highly Chlorinated Fullerene C₆₀Cl₃₀ with a Drum-Shaped Carbon Cage. Angew. Chem.Inf.ED, 44, 234 – 237.
- 20. Troshin, P.,A., Baskakov, S., A., Shulga, YU., M., Lyubovskaya, R., N., 2004. In the Chase of Mixed Halofullerenes: Remarkable Transformation of $C_{60}Cl_n$ (n= 6, 8, 12, 14) to $C_{60}Br_{24}$. Full.Nanot.Carb.-Nanostruct, 12, 159 – 163.
- 21. Govindaraj, A. and Rao, C. N. R, 2013. Functionalization and Solubilization of Graphene. J Nanomater Mol Nanotechnol, S1.
- 22. Park, J., Yan, M., 2013. Covalent functionalization of graphene with reactive intermediates. Acc Chem Res, 46, 181-189.
- Shanmugharaj, A. M., Yoon, J. H., Yang, W. J., Ryu, S. H., 2013. Synthesis, characterization and surface wettability properties of amine functionalized graphene oxide films with varying amine chain lengths. J Colloid Interface Sci, 401, 148-154.
- Marques, P. A. A. A., Golcalves, G., Cruz, S., Almeida, N., Singh, M. K., Grácio J. and Sousa, A. C. M., 2011. Functionalized Graphene Nanocomposites. Advances in Nanocomposite Technology, 374.
- 25. Zhang, K., Zhang, Y. and Wang, S., 2013. Enhancing thermoelectric properties of organic composites through hierarchical nanostructures.-Scientific Reports, 3, 3448.
- Kumar, R., Kumar, P., Naqvi, S., Gupta, N., Saxena, N., Gaur, J., Maurya, J. K. and Chand, S., 2014. Stable graphite exfoliation by fullereneol intercalation via aqueous route.New J. Chem., 2014.
- Zhang, X., Huang, Y., Wyng, Y., Ma, Y., Liu, Z. and Chen, Y., 2009. Synthesis and characterization of a graphene-C₆₀ hybrid material. Carbon, 47, 1, 334-337.
- 28. Zhang, Y., Ren, L., Wang, S., Mara the, A., Chaudhuri, J. and Li, G., 2011. Functionalization of graphene sheets through fullerene attachment. J. Mater. Chem., 21, 5386.