ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 6, pp. 1113–1116. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © S.D. Kushch, L.N. Blinova, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 6, pp. 941–944.

Sorption of Oxygen and Water by Fullerene Black from the Atmosphere

S. D. Kushch and L. N. Blinova

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
pr. Akad. Semenova 1, Chernogolovka, 142432 Russia
fax: (+7496)5241520
e-mail: ksd@icp.ac.ru

Received June 19, 2008

Abstract—Fullerene black stored in air, as well as fullerene[60], selectively sorbs oxygen and water. Upon the thermal desorption the adsorbed compounds are partially evolved in the unchanged form and oxidize the fullerene compound.

DOI: 10.1134/S1070363209060139

Earlier we mentioned [1] that fullerene black, which represents insoluble residual after exhaustive extraction of fullerenes from the product of electric-arc graphite vaporization in helium atmosphere (fullerene-containing soot), contains oxygen and water. The EPR study of fullerene black [2] shows that the dependence of the signal amplitude (I) of the fullerene black on the oxygen pressure P is described by the following formula:

$$\frac{I}{I_0} = \frac{n_1}{1 + P/K_1} + \frac{n_2}{1 + P/K_2}.$$

Here K_i and n_i are equilibrium constants and fractions ($n_1 + n_2 = 1$) for two centers of oxygen binding. In the cited works [1, 2] we could not make any suppositions about the nature of the centers of binding oxygen and water. Later we have shown that fullerene black selectively sorbs oxygen from air [3]. In the present work we shall consider the mechanism of binding oxygen and water by fullerene black.

Fullerene black obtained by the procedure [4], unlike ordinary soot obtained in production of fullerenes (pressure of helium 100–300 torr, inter-electrode distance 1–3 mm), contains no graphite (absence of reflexes at 2θ = 26.7°, Fig. 1, curve *2*). According to electron microscopy, particle size of fullerene black is 40–50 nm. Its conductance measured by a four-contact mode on the pressed plate is rather low (~0.03 Ω^{-1} cm^{-1}). Low conduction points to the absence of a developed conjugated system in the structure of the obtained "special" fullerene black.

Distinctions between "special" and ordinary fullerene black consisting in the absence of graphite and in the high concentration of non-conjugated double bonds, are manifest themselves in lower temperatures of oxidizing and in completion of the fullerene black oxidation before 670°C (Fig. 2). Graphite oxidation in ordinary fullerene black begins at 630°C, the maximum rate is reached at 700°C (Fig. 2, curve *3*).

According to the elemental analysis, fullerene black stored in air contains carbon, oxygen, and admixtures of hydrogen, but does not contain nitrogen and a solid

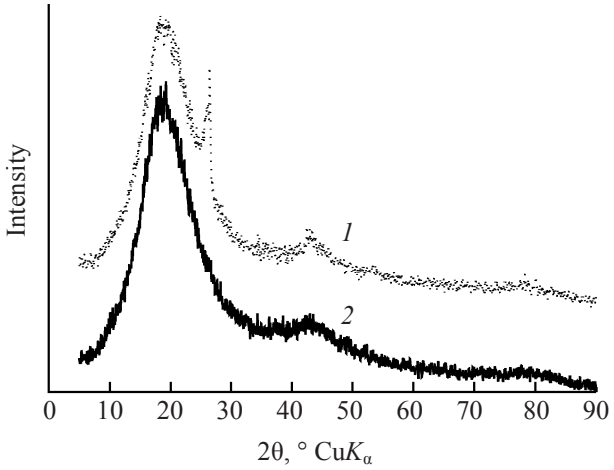


Fig. 1. Diffractograms of (*1*) ordinary and (*2*) "special" fullerene black.

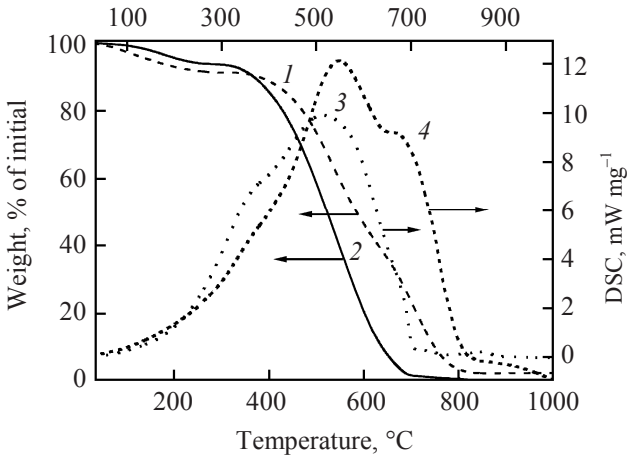


Fig. 2. Oxidative thermograms combined with DSC for (*1, 3*) ordinary and (*2, 4*) "special" fullerene black.

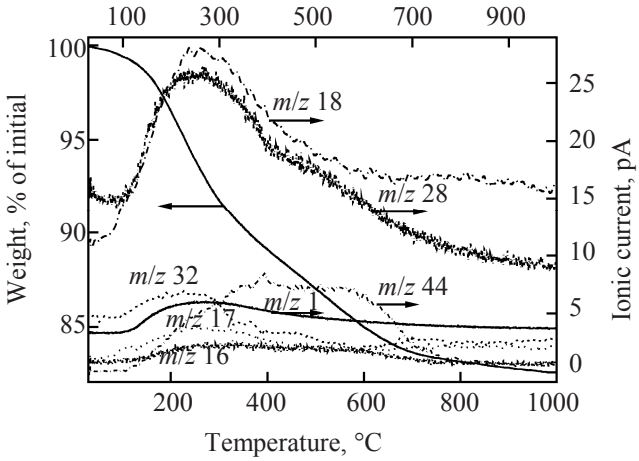


Fig. 3. Thermogram of fullerene black in argon atmosphere combined with mass spectral analysis of gaseous decomposition products.

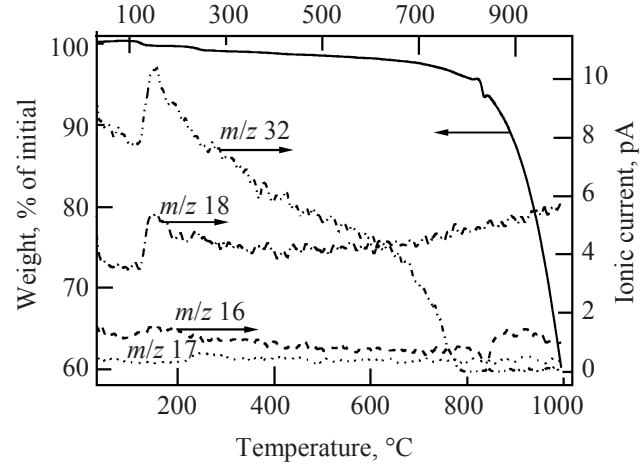


Fig. 4. Thermogram of fullerene C_{60} in argon atmosphere combined with mass spectral analysis of gaseous decomposition products.

residue. According to the X-ray photoelectron spectroscopy, surface layers of fullerene black include 91.0 wt % of carbon and 8.8 wt % of oxygen. These data confirm our assumption on the adsorption of oxygen and water from atmospheric air by fullerene black on storage.

Thermal analysis in argon flow combined with mass-spectrometry has shown that fullerene black stored in air (Fig. 3) mainly contains products with *m/z* 1, 2, 16, 17, 18, 28, 32, and 44.

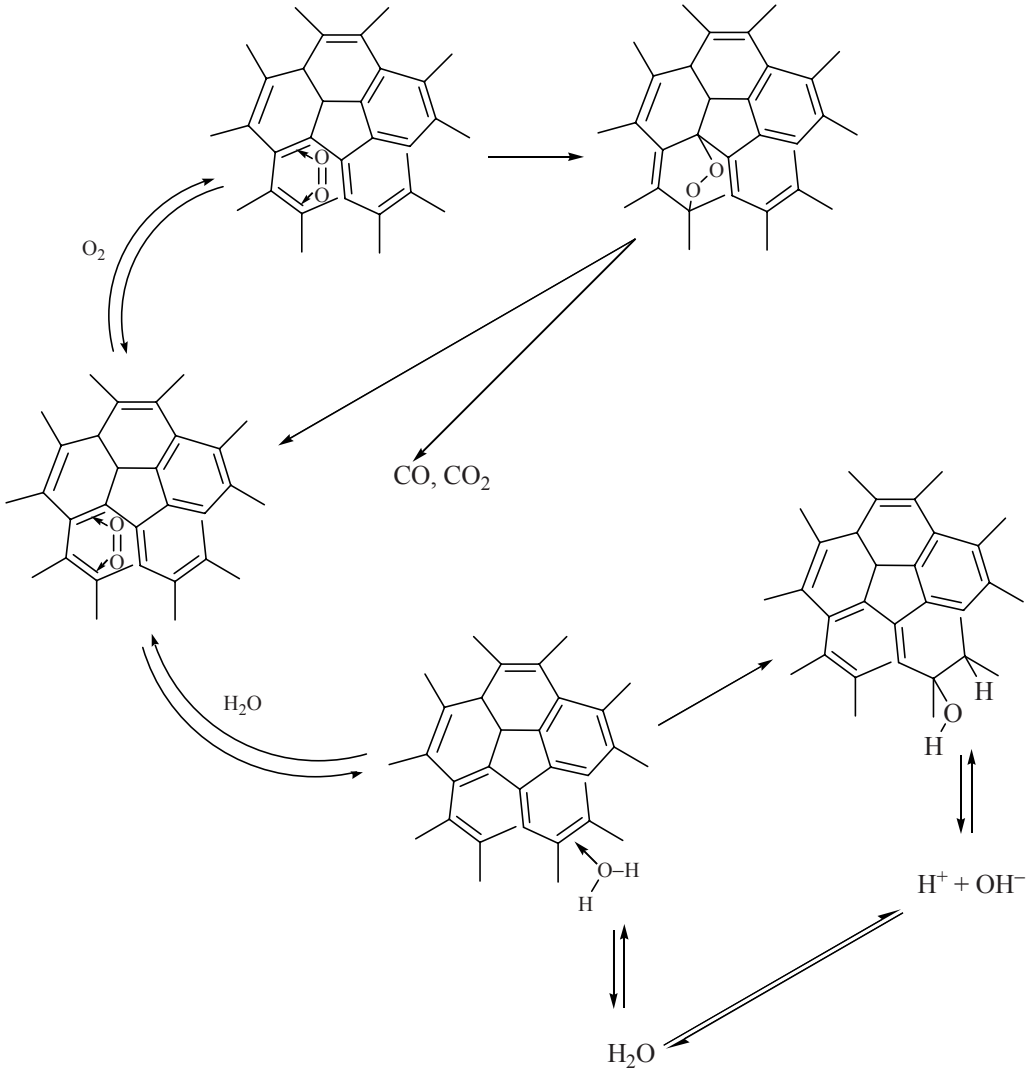
Oxygen adsorbed by fullerene black on storage in air is desorbed in the interval 100–400°C in unchanged form (*m/z* 32 and 16), but its considerable part is consumed for the oxidation of fullerene black up to carbon oxide (*m/z* 28) and dioxide (*m/z* 44). The observed fragment with *m/z* 28 is not nitrogen, as nitrogen is absent from fullerene black stored in air, and particles with *m/z* 14 usually formed at N_2 fragmentation were not detected in the mass spectrum. Carbon oxide is liberated in the intervals 100–370 and 350–620°C, and carbon dioxide, in the intervals 100–350 and 400–650°C. Probably, there are at least two types of oxygen adsorption centers, as indicated by unequal decrease off ionic currents for the peaks *m/z* 32 and 16 and two intervals of CO_2 liberation. The formation of carbon dioxide by the reaction of CO disproportionation $2CO \rightarrow C + CO_2$ is quite possible, which is proved by a decrease in the weight loss rate in the temperature interval 400–620°C. The formation of CO at an oxygen deficit is an ordinary phenomenon, but the temperature of fullerene black oxidation is lower than the normally observable temperature of the oxidation beginning in air flow (≥280°C).

In spite of hydrophobicity of fullerenes and fullerene black, noticeable amounts of water (*m/z* 18, 17, 1) are present in the products of the fullerene black thermolysis, and temperature of its thermal desorption exceeds boiling point of water. Taking into account the presence of non-conjugated double bonds in the fullerene black structure, we can assume that water is an acid in relation to them (an agent of HX type). It is also indicated (Fig. 3) by high values of ionic currents for the peaks *m/z* 1 and 17 (presumably H^+ and OH^-) and by low values for *m/z* 2 (not shown in Fig. 3).

Similar decomposition products are observed at the thermal analysis of fullerene[60] (Fig. 4) or a fullerene extract. According to the X-ray photoelectron spectroscopy data, fullerene[60] includes 99% of carbon and 1% of oxygen.

In the case of nanotubes and nanofibers with a graphene structure the thermal desorption of oxygen is not observed. The calcination of fullerene black in vacuum reduces the amount of sorbed oxygen, and the concentration of oxygen in surface layers decreases by 8.8% for the initial black and by 1.6% for the black annealed at 850°C within 8 h. Earlier we assigned such annealing effect to the straightening of curved carbon surfaces and to the formation of a system of conjugated bonds [2]. This assumption is supported by a rise of fullerene black conduction due to annealing, by the resulting decrease in the quality factor of the EPR instrument mentioned earlier [1, 2], and by difficulty of molding annealed black tablets. Graphite reflexes appear in diffractograms of fullerene black only as a result of roasting at 1200°C. Ordinary fullerene black contains much less oxygen than the "special" black containing graphite.

Thus, only fullerenes and fullerene black with a high concentration of non-conjugated double bonds (up to one double bond per three carbon atoms) selectively adsorb oxygen and water from air. According to the concept on the possibility of the interaction of electron-deficient fullerenes and fullerene black with electron-donor compounds, the possibility of binding oxygen mentioned earlier can consist in the further oxidation of fullerenes and fullerene black with the formation of their oxides [2]. The attachment of water, for example, due to a lone pair of the oxygen atom, i.e. by the coordination of electron-deficient fullerenes or fullerene black to the negative end of the water dipole, also fits in this concept. Possible conversions of the adsorbed oxygen and water molecules can be described by the following scheme.



The possibility of the back reaction of addition products with the formation of fullerenes is known. For example, oxides of fullerenes convert on heating to fullerenes [5.] Cyclic adducts of fullerenes also are inclined to the back detachment reaction (see, for example, [6, 7]). It was observed earlier that additions attached to fullerene black can be detached from the adducts, as it occurred, for the example, in the case of the bromo derivative, which is a brominating agent in the presence of covalent C–Br bonds [1].

In the present work we have shown that the reactions of oxygen and water addition to fullerenes and fullerene black are not thermally reversible, as they are accompanied by the carbon oxidation.

EXPERIMENTAL

Fullerene black was prepared from fullerene-containing soot synthesized by electric-arc graphite vaporization under special conditions providing its high specific surface area and reactivity [4]. Fullerenes were withdrawn by exhaustive extraction; their yield on the vaporized graphite was 8.3%. Under used conditions of the electric arc vaporization no more than 10% of cathode deposit is formed. The yield of fullerene black was 91%. All mentioned yields refer to the vaporized graphite. A sample of the fullerene C[60] of 99.92% purity was provided by the "Neo-TekProdact" firm (St. Petersburg, Russia). The thermograms were recorded on a STA-409 PC Luxx thermoanalyzer combined with a QMS-403 C (NETZSCH, Germany) mass-spectrometer. All m/e values are given in atomic weight units.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 08-03-01117).

REFERENCES

1. Kushch, S.D., Fursikov, P.V., Kuyunko, N.S., Kulikov, A.V., and Savchenko, V.I., *Eurasian Chemico-Technological Journal*, 2001, vol. 3, no. 2, p. 131.
2. Kulikov, A.V., Kushch, S.D., Fursikov, P.V., and Bogatyrenko, V.R., *Appl. Magnetic Res*., 2002, vol. 22, p. 539.
3. Kushch, S.D., Abstracts of Papers, *Trudy X Mezhdunarodnoi Konferentsii "Vodorodnoe materialovedenie i khimiya uglerodnukh nanomaterialov"* (Proc. X Int. Conf. "Hydrogen Materials Technology and Chemistry of Carbon Nanomaterials"), Sudak, 2007, p. 902.
4. Kushch, S.D., Muradyan, V.E., Fursikov, P.V., Kuyunko, N.S., Kulikov, A.V., Davydova, G.I., and Knerel'man, E.I., Abstracts of Papers, *Trudy VII Mezhdunarodnoi Konferentsii "Vodorodnoe materialovedenie i khimiya gidridov metallov"* (Proc. VII Int. Conf. "Hydrogen Materials Technology and Chemistry of Hydrides of Metals"), Alushta, 2001, p. 514.
5. Uchijima, Sh. and Kikuchi, Ya., Jpn. Patent Pending JP2004175598, *http//ep. espacenet.com*.
6. Llacay, J., Mas, M., Molins, E., Veciana, J., Powell, D., and Rovira, C., *Chem. Commun*., 1997, p. 659.
7. Ishida, H., Komori, K., Itoha, K., and Ohno, M., *Tetrahedron Lett*., 2000, vol. 41, p. 9839.