

# THE NUCLEOPHILIC ADDITION TO FULLERENE BLACK

**Kushch S.D.\***, **Kuyunko N.S.**

Institute of Problems of Chemical Physics of RAS  
1, Acad. Semenov's prospect, Chernogolovka 142432, RF

\*Fax (+7)(496)5241520, E-mail: ksd@icp.ac.ru

## Introduction

As recently we shown, fullerene black as like fullerenes contain double bonds, i.e. ones is an alkene [1]. The electrophilic addition reactions wherein on first stage alkenes double bond is attacked by positive ion as proton are typical for aliphatic series alkenes with increased electron density. Only alkenes containing electron-seeking group and conjugated bonds system undergo the nucleophilic addition reactions wherein alkene is attacked by negative ion. In the case of fullerenes as cage-like super-alkenes or similar to it non-closed fullerene black the addition type by this way can not be determined. In present work nucleophilic addition to fullerene black and possibility of its functionalisation are shown.

## Results and Discussion

The nucleophilic addition reactions are preferable reaction type for electron-seeking fullerenes and fullerene black. [60] fullerene as solution in toluene interacts with alkali aqueous solution in two-phase system with fullerol formation. Tetrabutylammonium hydroxide catalyses this reaction and is interphase transfer catalyst. Fullerene black as against [60] fullerenes, interacts with alkali without catalyst. At boiling 0.1 mg of fullerene black in 100 ml of 10 wt.% a solution of  $\text{Na}_2\text{CO}_3$  within 2 h not filtered, badly sedimentating suspension is formed. The solid phase of suspension, probably, represents a mixture of a hydroxyl derivative of fullerene black with its sodium salt. This solid phase easily oxidizes as contains, on analysis findings, 15-16 wt.% of oxygen and up to 7 wt.% of a solid (probably, sodium oxide).

The analogous pattern is observed at boiling of 0.1 g of fullerene black in 100 ml of 30 wt. % of NaOH solution within 2 h. Thus sodium salt of hydroxyl derivative of fullerene black also is formed. This salt contains less oxygen and oxidizes more difficultly. Boiling 0.1 g of fullerene black in 100 ml of water with the additive of pyridine ( $0.124 \text{ mole}\cdot\text{l}^{-1}$ ) during 2 h also results to formation of a hydroxyl derivative of fullerene black. Salt of hydroxyl derivative of fullerene black thus cannot be formed because pyridine is weak base ( $\text{pK}_b 8.82$ ). For the same reason the contents of oxygen introduced as hydroxyl groups,

is small and formed hydroxyl derivative of fullerene black roxyl derivant oxidizes more difficultly than products of interaction with  $\text{Na}_2\text{CO}_3$  or NaOH (fig. 1).

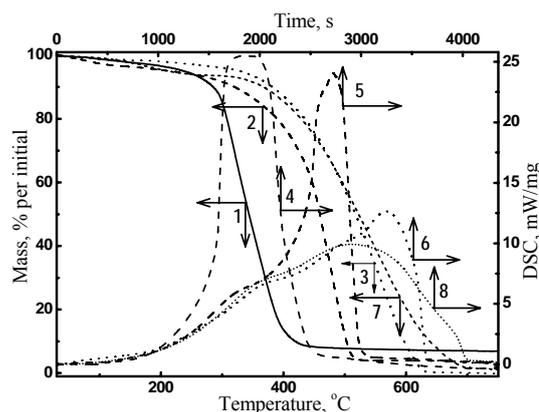


Fig.1. Oxydative thermograms and DSC curves of fullerene black (7, 8) and products of its interactions with solutions of  $\text{Na}_2\text{CO}_3$  (1, 2), NaOH (3, 4) and pyridine (5, 6).

IR spectra of a formed hydroxyl derivative of fullerene black (fig. 2) are characterized by wide absorption bands of hydroxyl groups at  $3432 \text{ cm}^{-1}$ , C=O bonds at  $1068 \text{ cm}^{-1}$  and double carbons - carbon bonds about  $1600 \text{ cm}^{-1}$ , is similar to spectrum IR of fullerol [2]. The absence of any groups, except for indicated, in products of interaction of fullerene black with  $\text{Na}_2\text{CO}_3$ , NaOH and with aqueous pyridine additionally specifies nucleophilic character of addition.

At the boiling of fullerene black in water its hydroxyl derivative is not formed. Analogously, hydroxyl derivative is not formed at boiling of fullerene black in benzene - water mixture wherein water is acid, i.e. the protons donor. Really, water with low concentration of hydroxyl-ion is not nucleophilic reagent. Fullerene black in opposite to alkenes does not interreacts with electron-seeking reagent as HCl. All this is quite stacked in a hypothesis expressed about nucleophilic addition to fullerene black.

The hydroxyl groups concentrations introduced by fullerene black boiling with different reagents within 2 h at the like temperatures differ from each other. These differences are concerned with nucleophilicity of reagents used at boiling. Really,

nucleophilicity in the first approximation is proportional to basicity and basicity of used reagents changes among  $\text{NaOH} \gg \text{Na}_2\text{CO}_3 > \text{PyH}$ .

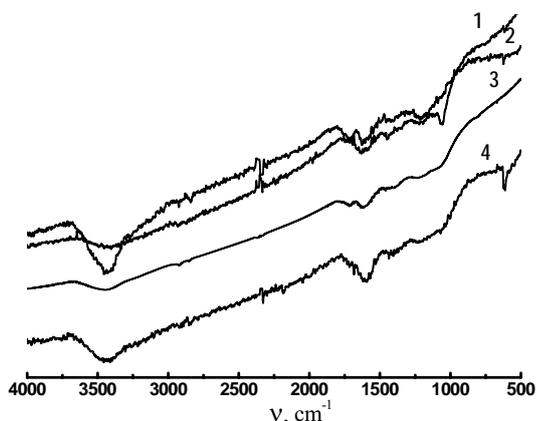


Fig. 2. IR spectra of a products of ineractions of fullerene black with solutions of  $\text{Na}_2\text{CO}_3$  (4), pyridine (3),  $\text{NaOH}$  (1) and ethanolamine (2).

Except for hydroxylation it is possible to realize addition of ethanolamine to fullerene black. Ethanolamine represents zwitter-ion and its addition proceeds as oxidative.

In IR spectrum of a product of ethanolamine interaction with fullerene black absorption bands of C-O bonds are observed at  $1068 \text{ cm}^{-1}$ , double carbons - carbon bonds about  $1600 \text{ cm}^{-1}$  and bonds C-N ( $1640 \text{ cm}^{-1}$ ) at absence of absorption band of OH-groups that confirms a cyclic structure of adduct (fig. 2).

## Conclusions

Observed hydroxylation of fullerene black by nucleophilic addition renders impossible quantitation of functional groups in the carbon materials containing fullerene black, main component as amorphous carbon (in particular, in nanofibers and multi-walled nanotubes) by Boehm's method [3, 4] inclusive carbon material titration by sodium hydroxyde, sodium carbonate, sodium ethylate and hydroxylamine.

## References

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