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Molecular theory of graphene oxide

Elena F. Sheka,* Nadezhda A. Popova

Peoples Friendship University of Russia

117198 Moscow, Miklukho-Maklay 6, Russia

*To whom correspondence should be addressed. E-mail: sheka@icp.ac.ru

Oxidation-induced structure transformation. The stepwise oxidation is followed by the gradual substitution of the sp^2 -configured carbon atoms by sp^3 ones. Since both valence angles between the corresponding C-C bonds and the bond lengths are noticeably different in the two cases, the structure of the carbon skeleton of the pristine (5,5) NGr molecule loses its planarity and becomes pronouncedly distorted. Comparing the pristine diagram with those belonging to a current oxidized species makes it possible to trace changes of the molecule skeleton structure.

Figs.S1a and b demonstrate the transformation of the skeleton structure in due course of both first-stage and second-stage oxidation exemplified by the changes within a fixed set of the C-C bonds of GO IV and GO VII. As seen in Fig. S1a, the OH-framing of GO IV causes a definite regularization of the C-C bonds distribution. None of single C-C bonds is formed since the chemical activity of edge atoms is not completely suppressed due to which $sp^3 - sp^2$ transformation does not occur. Contrary to this, the second-stage oxidation is followed by the formation of single C-C bonds that evidently prevail in Fig.S1b thus exhibiting a large-scale sp^3 sp^2 transformation. The appearance of the elongated C-C bonds, the number of which increases when oxidation proceeds, is naturally expected. However, to keep the skeleton structure continuous, this effect as well as changes in valence angles should be compensated. At the level of bonds, this compensation causes squeezing a part of pristine bonds. The plotting in Fig.S1b shows seven C-C bonds which are extremely short and whose lengths are in the interval of 1.345-1.355 Å. These lengths point to non-saturated valence state of the relevant carbon atoms which are not attached by oxygen, on one hand, however, on the other hand, are under the critical value of 1.395Å that put a lower limit for observation of the odd electron correlation [1]. Under this value, the bond length provides a complete covalent bonding of odd electrons due to which these electrons are fully correlated so that the total number of effectively unpaired electrons N_D is zero. The formation of these short bonds explains stopping of the oxidation reaction at the 52th step of the second-stage reaction.

Figure S1c presents the length distribution of C-OH and O-H oxidant given groups. Dark red plotting is related to GO IV and describes the bonds of framing atoms while gray plotting shows similar distribution in the case of the 74-fold GO VII. As seen in the figure, the bonds are quite regularly distributed in the both cases. The relevant dispersion of the bonds is listed in Table S1. The dispersion is bigger in the latter case but does not exceed 2% of the average value pointed in the table. As seen in the figure, all the C-OH bonds related to hydroxyl attached to the basal plane atoms are longer than those related to OH-framing of the molecule during the first stage of oxidation (1.417 and 1.371Å, respectively, see Table S1). Important to note that previously short C-OH bonds related to edge atoms elongate during the second stage of oxidation as well and approach the average length of 1.417 Å. At the same time, part of these bonds, which remain untouched during this stage, preserve their shorter lengths.

The transformation of the molecule skeleton structure in the case of the hetero-oxidant reaction is shown in Fig.S2. Figure S2a presents the skeleton distortion of GO V by the end of the first-stage oxidation. Since 20 carbonyls and two C-OH groups form the molecule framing, the dominant elongation of C-C bonds due to sp^3-sp^2 transformation provided by carbonyls is clearly seen Two C-OH groups leave the corresponding edge atoms in sp^2 configuration. The second-stage oxidation concerns two edge and 38 basal atoms. Shown in Fig. S2b exhibits the skeleton distortion by the 21st step of the second-stage oxidation for GO X. The dominant majority of bonds become single due to the large-scale sp^3-sp^2 transformation. The remaining untouched carbon atoms form bonds of 1.343-1.358Å in length similarly to the case shown in Fig.S1b. Reasons for these bonds creation are discussed above. As previously, the bonds length provides a complete covalent bonding of the remaining further oxidation. The appearance of shortened C-C bonds in GO VII and GO X, lengths of which are less than the critical value of 1.395Å, is quite similar to that takes place during the stepwise hydrogenation [2] and fluorination [3] of fullerene C₆₀.

Figure S2c discloses events that concern attached oxidants. As said above, the first-stage oxidation is terminated by a complete framing of the pristine molecule by 20 carbonyls and two hydroxyls. Consequently, dark red curve in Fig.S2c exhibits 20 C=O bonds as well as two C-OH and two O-H bonds of GO V. Gray curve presents the bond structure after terminating of the second-stage oxidation for GO X at the 21st step. As seen, previously much shorter C-OH bonds of 1.348Å lengthen up to 1.413Å and are comparable by length with all the newly formed C-OH bonds; C=O bonds differ slightly, and C-O-C bonds of epoxide groups are added. The average length values are listed in Table S1 alongside with the bond length dispersion. As seen in the table, the bond distributions are quite homogeneous and their dispersion does not exceed 1%.

References

- 1. E.F.Sheka and L. A. Chernozatonskii, Int. J. Quant. Chem., 2010, 110, 1466-1480.
- 2. E.F. Sheka, J. Mol. Mod., 2010, 17, 1973-1984.
- 3. E.F. Sheka, J. Exp. Theo.r Phys., 2010, 111, 395-412.

GOs ¹	C-O bonds lengths, Å				
	С-ОН	0-C-0	C=O		
First-stage oxidation					
Ι	-	-	1,234 (5.30; - 0,90)		
II	1,372 (0.70; -0,30)	-	1,249 ²		
III	1,362 (3.79; -0.99)	-	1,233 (0.58; -0.47)		
IV	1,372 (0.46; -0,33)	-	-		
V	1,348 (0.43; -0.43)	-	1,233 (1.04; -0.83)		
	Seco	ond-stage oxidation			
VI (II) ³	1,368 (2.10; -4.01); 1,419 (1.85; -1.39)	-	1,230 ⁴		
VII (IV)	1,371 (0.32; 0.18) 1,417 (1.98; -1.68)	-	-		
VIII (I)	-	1,434 (0.20; -0.27)	1,234 (0.27; -0.21)		
IX (I)	1,417 (0.29; -0.14)	1,438 (0.38; -0.46)	1,223 (0.42; -0.38)		
X (V)	1,413 (1.08; -0.46)	1,436 (0.24; -0.46)	1,223 (0.63;-0.30)		
XI (I)	$ \begin{array}{c} 1,417;\\ 1,354^5\\ (0.24;-0.22) \end{array} $	1,437	$1,230^{5}$ (0.25; -0.27)		

Table S1. Average bond	l lengths of the	5, 5) NGr oxides and	their dispersion, %
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¹Oxides under the corresponding numbers are presented in Figs. 2, 3, 7,8, 10, and 12. ² A solitary C=O bond, see Fig.2 ³ Here and below the figures in brackets point the reference to GOs of the first-stage reaction. ⁴ A solitary C=O bond, see Fig. 8 ⁵ The data related to the COOH oxidant.

Figure captions

Figure S1. The sp^2 - sp^3 transformation of the (5, 5) NGr molecule skeleton structure in due course of the successive homo-oxidant oxidation; the C-C bond length distribution after the first-stage oxidation, GO IV (a) and the second-stage oxidation, GO VII (b). Light gray histogram is related to the pristine molecule. c. Oxidant-given C-O(H) and C-H bonds at the first-stage (dark red) and the second-stage (gray) oxidation.

Figure S2. The sp^2 - sp^3 transformation of the (5, 5) NGr molecule skeleton structure in due course of the successive hetero-oxidant oxidation; the C-C bond length distribution after the first-stage oxidation, GO V (a) and the second-stage oxidation, GO X (b). Light gray histogram is related to the pristine molecule. c. Oxidant-given C=O, C-O-C, C-OH and O-H bonds at the first-stage (red) and the second-stage (gray) oxidation.



Figure S1



Figure S2