Acidity of graphene oxide aqueous solutions: 
the origin unveiled

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Abstract
Nonempirical modeling of hydrated single-layer graphene oxide (GO) fragments revealed that the probable origin of the acidity of aqueous GO solutions is the dissociation in closely grouped hydroxyls. The process is further promoted by the adjacent $\pi$-conjugated carbon subsystem at the edges of GO flakes or their inner defects. The apparent $pK_a$ values of the groups fall in a range of ca. 2.0 to 5.3.

Nowadays, graphene oxide (GO) may seem too old to be of a valuable theoretical interest, the more so as the characteristics of the material vary depending on the method of synthesis [1], which makes a task of elaborating a reasonable universal model of its structure practically unsolvable. Hence, any question related to the structure peculiarities seems ill defined. At the same time, there is a unique property of any GO specimen unclarified up to the present moment, namely, the high acidity of its aqueous solutions. [6,7] According to the titration data for different GO specimens, there should be about 1 acidic site per each 17 carbon atoms [2]. This means that each tetrad of carbon hexagons should contain an acidic site with a roughly estimated $pK_a$ value of 3.93–3.96 [2], which is too high for typical carboxylic groups that are not as numerous in non-degraded GO specimens, and the more so for the prevailing individual hydroxyl groups [1]. As a kind of a compromise, vynilogous acids were suggested [2] to be key groups in this respect, but to our mind the corresponding elegant dynamic model, which quite reasonably acquires for the disintegration of GO specimens in water, cannot account for the existence of numerous quite closely arranged acidic sites on non-degraded GO flakes almost immediately upon their formation.

To solve the problem one needs detailed information about the correlation between variations in the contents and local arrangements of oxygen-containing functional groups and the observed acidity of GO specimens. This by no means can be done in terms of purely experimental approach for nobody can state that not only the arrangements of functional groups but even the relative amounts of diverse groups are known. The qualitative and partly quantitative information of the latter kind can be retrieved from NMR, FTIR, or XP spectra, but even these data are far from unambiguity due to the variations in the peak positions of particular functional groups depending on their neighborhoods, including adjacent segments of carbon layer and water molecules. [3–5] Therefore, simulations of model systems, which involve diverse combinations of functional groups bound to the surface and edges of a carbon fragment, seem to be the only way that may help in clarifying the origins of the acidity of aqueous GO solutions. We have considered various models and found those very...
combinations that may determine the acidity; and the origin seems unexpected at first glance, but quite reasonable upon a closer view and very interesting for the chemistry in general.

To construct models, we took into account the experimental data and theoretical concepts of GO structure [1]. In GO specimens prepared according to the most widely used original or modified Hummers techniques, the oxidized-to-graphitic carbon ratio varies from 61:39 [8] to 69:31 [9]. Areal estimates of the highly disordered oxidized regions, non-oxidized graphitic domains, and defects provided reasonably close values of 82, 16, and 2%, respectively [10]. The surfaces of GO flakes are negatively charged as follows from the high absolute values of the negative ζ-potential, which is nearly by half larger for the most deeply oxidized specimens. [10] This fact additionally substantiates the relatively high dissociation constant of some functional groups in GO and prompts one to combine the basic ideas of Lerf and Klinowski [11], Scholtz and Boehm [12], Szabo and Dekany [13], and Dimiev, Alemany, and Tour. [2]

To minimize the systems, basal carbon plane fragments were decorated chiefly with the groups that can act as proton donors or assist the process, which are carboxyls and carboxylics along edges and hydroxyls anywhere. Sin location of hydroxyls was not considered because the high inner strains that accompany their appearance should inevitably lead to either rearrangement or bond-breakage reactions; and only anti hydroxyl pairs can be thought of as relatively long-lived. The C/O ratio was varied approximately from 3:1 to 3:2, the latter one corresponding to a slightly larger oxygen content compared to the aforementioned averaged figures, but taking into account that we do not treat the graphitic and defect domains, and model strictly one layer (whereas experimental estimates reflect some averaged data for one and several-layer flakes), such variations in the integral composition are quite founded. Nonempirical simulations were carried out in the cluster approach because in real specimens there is no regularity and periodicity in the spatial arrangement of both oxidized and unoxidized carbon domains, as well as the decorating functional groups within the oxidized domains; and the effects related to the proton-donating ability seem to be of a relatively short-range nature. For solving the electronic problem, the density functional method with the B3LYP hybrid functional was selected along with the double-ζ Gaussian basis set of 6-31G quality for basal plane carbon atoms and 6-31G(d,p) for all the residual atoms involved in functional groups and water molecules. Such combined basis set complies with the requirements to the sets used for simulating 2D or 3D objects (particularly, it is sufficiently compact to avoid linear dependence of basis functions when describing systems that involve up to two hundreds closely arranged atoms) and provides a balanced description of the grafted groups (it is sufficiently flexible due to the same large number of atoms, the tails of the atomic functions of which contribute to the description of the electron density distribution in their both more and less distant neighborhoods). The basal plane fragment involved 30 to 54 carbon atoms; the numbers of hydroxyl, carbonyl, and carboxyl groups were varied in ranges of 5–20, 1–3, and 1–5 respectively, and the number of water molecules was varied from 5 to 35. The correspondence of the structures to local minima of the
adiabatic potential was confirmed by the normal-coordinate analysis; and thermal effects were tentatively taken into account by estimating the Gibbs energy increments (at 298K) determined solely by the vibrational degrees of freedom ($G_{\text{vib}}$), which is possible because differences between the $G_{\text{rel}} = E_e + G_{\text{vib}}$ relative values counted from the selected potential energy minimum (which are of primary importance to us) reflect only the changes related to some local internal structure transformations, when contributions of most of the degrees of freedom are nearly canceled out. Formal logarithmic equilibrium constants of the possible dissociation reactions ($pK_a$) were estimated based on $-\Delta G_{\text{rel}}/RT$. Simulations were carried out with the use of Firefly 8.2 package [14] and visualized with Chemcraft software. [15]

Based on the results obtained, the most spectacular $C_{27}H_6(O)(COOH)_{3}(OH)_{15} \cdot (H_2O)_n$ composition with a varying number of water molecules, $n=5$–35, was constructed and considered in detail below. In the model GO fragment (which is sufficiently deeply oxidized to acquire a typical folded profile), hydroxyls arranged over the basal plane and along its edges are grouped in diads, triads, and pentades. At the largest considered number of water molecules, $n=35$, there are a complete hydration monolayer over the functional groups at one side of the carbon plane and an extended hydration sphere around one edge OH triad (Fig.1a). As can be seen, hydroxyls, which reside in the central part of the carbon fragment, form hydrogen bonds with each other so that water molecules are not included in the corresponding H-bond sequence but rather attached to it from above (a1 in Fig.1). Note that there is one hydroxyl (encircled) that acts as an acceptor of two H-bond protons of the neighboring hydroxyls and a donor of its own proton in an H-bond to a water molecule. In the case of the edge hydroxyls (a2 in Fig.1), their larger freedom in the relative orientation results in the formation of an H-bond network, in which they are interspersed with water molecules though a certain orientation again toward one OH group (encircled) can be noticed. It is these highlighted OH groups that are the best candidates for the dissociation.

In the case of the hydroxyl in the central part of the carbon segment, a stable configuration that involves a water separated $(C)O^-\cdots(H_2O)\cdots H_3O^+$ ion pair was found (b1 in Fig.1); and its adiabatic potential energy is only 2.5 kcal/mol higher than that of the original neutral structure. When thermal energy increments are taken into account, the resulting difference between the Gibbs energies becomes only slightly larger, 2.7 kcal/mol, which formally corresponds to the $pK_a$ value of the hydroxyl dissociation of 2.0. This value is very high due to the stabilization of the $(C)O^-$ provided by the ordered H-bond sequences of hydroxyls that converge to this very oxygen in a nearly coplanar ring-like structure, which is stable due to the coordinating carbon footing.

In the case of the edge hydroxyl, the situation is visually similar but quantitatively different. The group can also lose a proton to produce a more distant hydronium ion, the shortest separations of which involve three water molecules: $(C)O^-\cdots(H_2O)_3\cdots H_3O^+$ (c2 in Fig.1). Again, the $(C)O^-$ group acts as a tricoordinate knot in the H-bond network, but here the stabilization of $O^-$ is provided by
Figure 1: Hydrated graphene oxide model $\text{C}_{27}\text{H}_6(\text{O})(\text{COOH})_3(\text{OH})_{15} \cdot (\text{H}_2\text{O})_n$ at (a,b,c,d) $n = 35$ and (e) $n = 25$: (a1, b1) central and (a2, c2) edge fragments of the model system (a, a1, a2) before and (b1, c2, d) after the dissociation of hydroxyls; (a, e) top and (d) side view of the model systems. Encircled are hydroxyl groups that can undergo dissociation and the resulting $\text{O}^{\delta-}$ and $\text{H}_3\text{O}^{\delta+}$ fragments.

its involvement in the 10-atomic $\pi$-conjugated carbon system, which should produce a stronger effect compared to the above H-bond network solely. And the strength is unexpectedly high: the adiabatic potential energy of the dissociation is negative! It equals $\sim 4.9$ kcal/mol, and $\Delta G_{\text{rel}}$, though smaller in absolute value, is also negative (-2.5 kcal/mol), which means that the dissociation of such edge hydroxyl groups is thermodynamically favorable, and the corresponding formal equilibrium constant is of an order of $10^2$.

Furthermore, the complementary stabilization of the two deprotonated hydroxyl groups, one at the edge and another, over the basal carbon plane, makes their coexistence energetically possible. Even within the small model fragment we consider, a configuration where both groups lost their protons to form water separated ion pairs was found (Fig.11), which complies with the aforementioned estimate of one acidic
site per each tetrad of carbon rings. Remarkably, the adiabatic potential energy of this double zwitterionic configuration is only 4.5 kcal/mol higher than that of the all-neutral structure, and $\Delta G_{rel}=4.8$ kcal/mol. The resulting polarization of the system can be referred to as altitudinal, or normal to the mean carbon plane, rather than longitudinal for irrespectively of whether any one or both hydroxyls dissociate, the corresponding hydronium ions are located nearly accurately over the oxygens of the parent hydroxyls.

The a priori unexpected thermodynamic favorableness of the dissociation of an edge hydroxyl has brought us to an idea of analyzing the process in more detail. When the number of water molecules in the model system is $n=25$, a spontaneous dissociation of the group was found to take place, and an $\text{O}^-\ldots\text{H}_3\text{O}^+$ contact ion pair appears (Fig. 1). A reason for that may be the following. At this number of water molecules, the edge hydroxyl triad is yet similar to the one over the carbon plane in that these hydroxyls form a directional H-bonded sequence, but it is not parallel to the carbon footing, rather coplanar to the aforementioned conjugated 10-atomic sequence. Insofar as hydrogen bonding is actually a complex $\sigma/\pi$ electronic bonding, the $\pi$-electronic contribution provides a kind of conjugation in H-bonded sequences on a condition that covalent and hydrogen bonds are alternating. As a result, here a usual $\pi$-conjugation within the subsystem of second-row elements (basal carbons and an oxygen anion) is supplemented with the H-bond conjugation, which assists in the dissociation and proton migration.

Thus, within at least triads of hydroxyls, where two groups as proton donors assist the third one, this latter can lose a proton irrespectively of whether it is located at the edge or over the basal carbon plane of a GO flake. The process may become spontaneous at a moderate hydration when the hydroxyls are bound to an incompletely oxidized edge of a carbon sheet. The dissociation of a hydroxyl located on a basal carbon plane can be characterized by apparent $pK_a$ values of about 2.0 in the absence of the neighboring dissociated groups and up to 5.3 when there is already a $(\text{C})\text{O}^-\ldots\text{(H}_2\text{O})_k\ldots\text{H}_3\text{O}^+$ ion pair in its relatively close proximity. The two hydration spheres around the edge hydroxyl and the average distance between the mean carbon and water planes of ca. 5.1 Å (which corresponds to the GO layer separation no smaller than 9 Å) in our simulations makes the predictions quantitatively reliable. And the result is of a principal importance to the chemistry of not only GO, but any extended carbon-based highly hydroxylated systems, such as e.g. humic substances.

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