

# PHYSICAL CHEMISTRY OF CARBON SURFACES: APPLICATIONS AND FUNDAMENTALS

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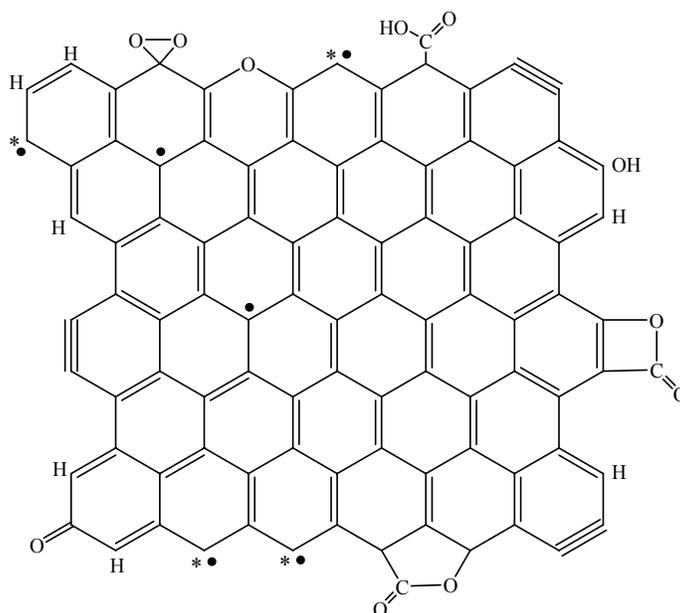
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## Introduction

A good understanding of the physical chemistry of carbon surfaces requires combined knowledge (i) of the nature of free graphene edge sites, (ii) of the nature and quantity of surface functional groups on these edge sites, and (iii) of their unique amphoteric character. This then allows one to understand the behavior of carbon materials in a remarkably wide range of applications: as reactants in oxidation protection, gasification or combustion, as adsorbents in purification of gaseous and liquid effluents, as high-surface-area supports for heterogeneous catalysts, and even as catalysts in their own right (Radovic, 2003). The key to the achievement of this goal is an 'interdisciplinary' (rather than 'multidisciplinary') approach, judiciously using the tools of both physics and chemistry. Conversely, the main obstacle in this process has been an excessive compartmentalization of knowledge, with the 'chemists' not fully appreciating or even being unaware of the advances made by the 'physicists', and *vice versa*. Almost a century ago, Paul Dirac did proclaim that the "underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are ... completely known" (Dirac, 1929). But, even though for quite some time any issue of the *Journal of Physical Chemistry* has not differed much from an issue of the *Journal of Chemical Physics*, and the name of the analogous European journal is *Physical Chemistry Chemical Physics* (yes, just like that), it has been only recently that quantum mechanics has provided chemically meaningful, relevant and trustworthy results. While many important details remain to be sorted out, both experimental chemistry and quantum mechanics are now yielding an arguably coherent and internally consistent picture of these three mutually interdependent features of the carbon surface. Here is a brief outline. A more extensive account is in preparation (Radovic, 2007).

## Surface Functional Groups

Historically this has been the earliest issue and the most extensively investigated topic. The pioneering work of Garten and Weiss (Garten, 1955; 1957a; 1957b; 1959) and of Boehm and coworkers (Boehm, 1959; 1965; 1966) has been the most influential. The ubiquitous oxygen-containing groups have received the greatest attention not only because oxidation has been the most popular tool for deliberate chemical modification of carbon surfaces but also because exposure of carbons, especially the high-surface-area ones, to room-temperature air often modifies significantly their chemical behavior. Figure 1 summarizes schematically our current understanding of the most important functional groups capping the graphene edges (together with related features discussed below).



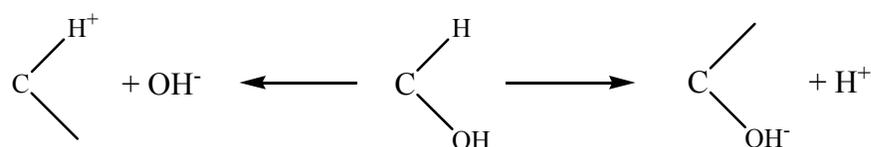
**Figure 1.** Key features of surface chemistry of a graphene layer in flat  $sp^2$ -hybridized carbons.

More recently, there has been an explosion of relevant research using carbon nanotubes and fullerenes, in the pursuit of purification protocols and multiple surface functionalization benefits. When the “dust settles”, it will be interesting to see whether curvature is responsible for any significant differences; thus, for example, even though Banerjee and coworkers (Banerjee, 2003) state that “[o]xidative processes used to purify nanotubes are capable of generating a variety of oxygenated functional groups ... at structural defect sites along the tube walls etched by the oxidizing agent”, they (Banerjee, 2002) and many other researchers postulate the interaction of such agents (e.g., O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>) not with defect sites but with basal-plane carbon atoms; this is contrary to the acknowledged relative chemical inertness of the basal-plane sites in flat graphenes.

Surface groups containing other heteroatoms are also of interest, but they have been neither explored nor are as well understood as the oxygen functionalities. Nitrogen functionalities are particularly attractive. For example, reports of their beneficial effect in reactions catalyzed by carbons have been persistent (Stöhr, 1991), and some are many decades old (Rideal, 1926; Larsen, 1940; Bente, 1943), but a general and consistent explanation of their role has yet to be formulated.

### ***Amphoteric Character of Carbon Surfaces***

Some of the functional groups on graphene edges can easily give rise to surface charge (e.g., COO<sup>-</sup>). This has been known since at least the 1930s, when King (1935) reported a monotonic rise in the pH of a charcoal suspension with increasing temperature of charcoal activation in a stream of moist oxygen; following Frumkin’s proposal that carbons can function as reversible electrodes, he postulated the following participation of surface functional groups:



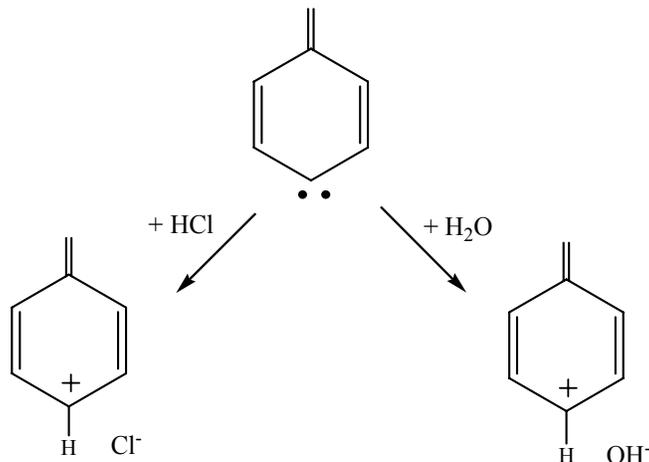
King did acknowledge that “the origin of the hydrogen and hydroxyl ions ... is obscure”, but an analogous protonation/deprotonation scheme was soon adopted as an explanation for the amphoteric character of carbons, e.g.,



It took more than half a century to rectify this notion and clarify the unique amphoteric character of carbon surfaces in aqueous solutions: even though there are some oxygen-containing groups (e.g., pyrones) with a basic character (Menendez, 1999) that confer a positive charge to the carbon surface below its isoelectric point, the Lewis base character of the π electrons within a graphene layer is now acknowledged to have an important contribution (Leon y Leon, 1992):



Carbene sites (see below) also exhibit basicity, as follows:

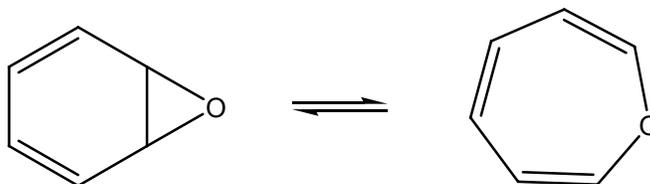


And although the concept of the isoelectric point of a carbon, or its point of zero charge (Menéndez, 1995), has been known since the 1920s (as cited by King, 1935), its important implications for the use of carbons as catalyst supports and liquid-phase adsorbents have been clarified only in the last decade (Radovic, 1997; Radovic, 2001a), inspired by a seemingly unrelated electrophoretic mobility study of chemically modified and weathered carbon blacks (Lau, 1986).

## Nature of Edge Sites

Ever since Rosalind Franklin proposed the still venerable models of graphitizable and nongraphitizable carbons (Franklin, 1951) the chemical nature of graphene edges (undefined ‘wiggles’ in Franklin’s cartoons) has been essentially “swept under the rug”, even though much effort has been expended in developing methods to quantify the number of active or reactive sites on carbon surfaces (Radovic, 2001b). Before the nature of these chemical linkages can be elucidated, and certainly before one prematurely succumbs to the temptation of ‘seeing’ curvatures (e.g., pentagons) even in cokes, chars, activated carbons and carbon blacks, we must agree on the structure of zigzag and armchair sites. Many of these are known to be oxygen-free (Menendez, 1996; 1997), and yet they are neither free radicals nor H-terminated, as is too often assumed. We have recently provided arguably compelling albeit circumstantial evidence that free zigzag sites are carbene-like while free armchair sites are carbyne-like (Radovic, 2005). A particularly useful feature of this proposal, which is still largely ignored by the “carbon physics” community, is that the triplet ground state of the carbene sites offers a simple (and elegant!?) explanation for the intriguing ferromagnetic behavior of some impurity-free carbon materials. Another of its virtues is that it allows us to address issues whose resolution has been heretofore impossible.

Thus, for example, the mechanism of formation of CO<sub>2</sub> is surely one of the key unresolved fundamental issues in carbon oxidation, combustion and gasification, with a multiplicity of very important practical implications. The approach adopted in our study is based not only on the use of quantum chemistry to explore the analogies with prototypical organic reactions, but also on well established experimental facts from carbon surface chemistry. The two reactions of primary interest are C + O<sub>2</sub> = CO<sub>2</sub> and C + 2NO = CO<sub>2</sub> + N<sub>2</sub>. They are analyzed with the Gaussian 03 software, using B3LYP/6-31G(d) model chemistry and representative two-dimensional graphene clusters. Adsorption at both armchair (carbyne) and zigzag (carbene) sites is considered. Among the many interesting results is the apparent requirement for (NO)<sub>2</sub> dimer interaction with the zigzag sites in an O-down configuration. For the carbon-O<sub>2</sub> interaction, of principal interest are the direct and indirect routes for CO<sub>2</sub> production: the former involves nondissociative adsorption on the carbene sites, while the latter includes the presence of mobile epoxide oxygen on the basal plane and its insertion into an edge hexagon, remarkably analogous to benzene oxide/oxepin valence isomerization, as illustrated below.



## Acknowledgments

The collaborators and colleagues to whom I am indebted for their help in developing and shaping the concepts summarized here, and explored during the past quarter of a century, are too many to acknowledge here. This research has truly been a collective effort, and I cannot emphasize enough the importance of the stimulus provided by reading the broad and relevant literature and by discussions at and around the many conferences that we have attended together in our pursuit of a better understanding of the remarkably chameleonic carbon surfaces.

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