QUANTUM CHEMISTRY OF GRAPHENE EDGES: PROGRESS, COMPARISON WITH EXPERIMENT AND CHALLENGES

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Introduction

The well documented heterogeneity (and complexity!) of carbon surfaces exposed to ambient air is due to the presence of carbon-oxygen surface complexes that at any given time and temperature are either 'spectators' or reactive intermediates [1]. The former are identified as the carbon *active sites* [2, 3]: oxygen is chemisorbed on them, but CO or CO_2 is not necessarily desorbed during the average surface reaction turnover, and at least temporarily stable surface complexes are thus formed. The latter are more precisely referred to as the *reactive sites* [4]. In the heterogeneous catalysis literature, the analogous distinction is between catalyst and catalytic sites [5]; it is the cause of *structure sensitivity* of catalytic reactions [6]. Experimental distinction and quantification of these sites has been a formidable challenge. A quantum chemistry approach [7] is beginning to yield interesting and promising results. Here I summarize some recent progress, with particular emphasis on the thermodynamics of nascent site deactivation. In the voluminous literature on the kinetics of reactions involving a wide variety of carbon materials, there are persistent though largely disconnected reports of a reactivity decrease with time, often referred to, rather vaguely, as 'aging'. In the exploding graphene physics literature, the related issue of edge reconstruction has been discussed recently. For example, Volnianska and Boguslawski echoed the findings of Koskinen and coworkers [8-10] that the "zigzag edge is unstable with respect to reconstruction consisting in the formation of a pentagon and a heptagon from two adjacent hexagons" [11] and concluded that the "question of the relative stability of the various terminations … awaits a definite answer"; but they failed to consider triplet ground states [12] in their own analysis of magnetism in graphene ribbons. Arguably, the key neglected issue is the fate of the unpaired σ and/or π electrons [12, 13].

Computational Methodology

Commercially available Gaussian03 software (www.gaussian.com) was used. Charge localization and delocalization effects and spin density distributions are compared in prototypical 2D graphene clusters; vibrational frequencies are calculated and energies and enthalpies of the ground and transition states are thus obtained. Because comparative effects and qualitative trends are of main interest, results were obtained using primarily the classical Mulliken population analysis.

Results and Discussion

As a reference, based on distributions in polyaromatic hydrocarbons (PAHs), the following ranges of (negative) charge densities are typically obtained on the four types of edge carbon sites:

| zigzag	zz cusp	armchair	ac cusp
0.30-0.37	Ca: 0.20-0.24	0.19-0.23	Ca: 0.18-0.21
	Cb: 0.12-0.13		Cb: 0.13-0.14
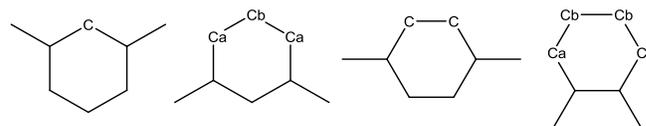
In contrast to PAHs, graphene edges are not all H-terminated [12], and certainly not the (re)active sites: there is increasingly compelling evidence [12-14] that the free armchair sites are singlet carbynes and the free zigzag sites are triplet carbenes.
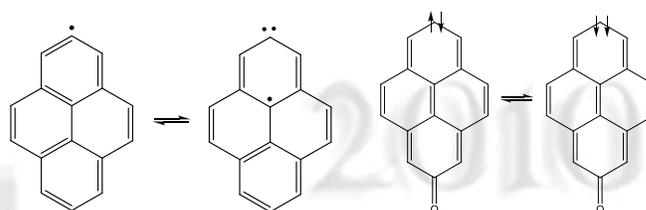
Fig. 1 Schematic representation of the nascent site deactivation (NSD) process: localization of a π electron to form an "in-plane sigma pair", i.e., a carbene site, in $C_{16}H_9$ (left) and singlet/triplet transition in $C_{16}H_8O$ (right).

The electron density localization at the triplet carbene site(s), illustrated in Figure 1, is analyzed in Figure 2. Such calculations offer, for the first time, a quantum chemical interpretation of the popular but intuitive concept of the "in-plane sigma pair" [15]. The energy difference between the ground-state triplet and the singlet state is 12.3 kcal/mol in the case of dehydrogenation of a C_a edge site, and 5.6 kcal/mol in the case of dehydrogenation of a C_b edge site; the corresponding thermodynamic driving forces for H abstraction, in terms of Gibbs free energies, are only slightly different, though, 101.0 and 102.5 kcal/mol. The greater stability of the C_a carbene structure is manifested also in a greater degree of electron localization: 1.3 electrons (Figure 2b) vs. 0.85 electrons (not shown). Abundance of such triplet states at zigzag edges in graphene [12, 14] has been offered [12] as a straightforward explanation for persistent reports of ferromagnetic behavior of some carbon materials. Upon further dehydrogenation, the degree of σ-π electron interaction depends on the H-removal site, with preference for electron localization being greater at C_a sites.

Ever since the electron spin resonance (ESR) technique has shown that carbons exhibit intriguing free-radical behavior, the origin and relative importance of localized and delocalized
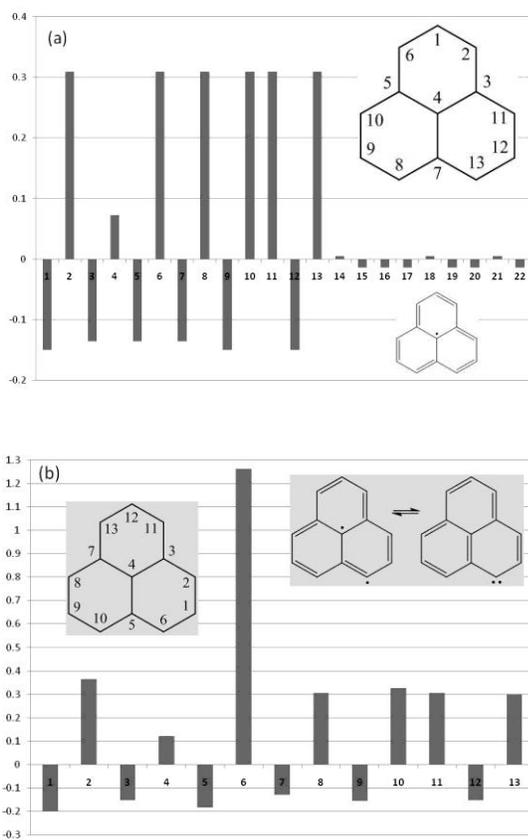
Fig. 2 Distribution of spin densities in a three-ring graphene cluster: (a) $C_{13}H_9$ (doublet); (b) $C_{13}H_8$ (triplet, H missing from a C_a site, only C atoms shown).

spin centers has been a matter of considerable controversy, for over half a century now. Indeed, some of the well established experimental facts have yet to be understood. In particular, a reconciliation of their 'physical' and 'chemical' interpretation is long overdue, ever since the pioneering but isolated (and almost entirely ignored!?) attempt by Weiss [16]. In an effort to reconcile the fact that "the onset of electrical conductivity at carbonization temperatures of 600-700 ^{o}C is accompanied by a rapid loss in free electron spins", he postulated that the following type of process is involved in the well documented appearance of p-type semiconductivity:
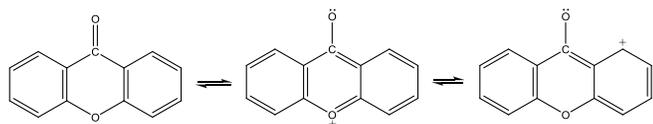
Because most carbons become predominantly basic upon heat treatment above ca. 700 ^{o}C, and consistent with the author's proposal that such basicity is due to carbonyl groups associated with chromene-like structures, the above scheme suggests that "the carbonyl group functions as an electron trap". While this proposal does offer a "satisfactory reason ... why the electrons should jump into the σ-traps only above a

certain temperature", and because carbon basicity is also due to the presence of oxygen-free sites, an equally satisfactory explanation – and one that is much more consistent with everything we know about carbon surface chemistry [12, 13] – is offered here: as the aromatic C—H bonds are broken, and this indeed becomes a dominant carbon-formation process above 600-700 ^{o}C, those edge carbon atoms that do not participate in condensation or repolymerization reactions (and thus in graphene growth) are stabilized by virtue of formation of carbene sites, whose σ-π interaction results in the formation of holes in the emerging conduction band and thus to p-type semiconductivity; such sites are also responsible for carbon basicity.

Additional quantum chemical details of the processes of unpaired electron localization, edge reconstruction, as well as the mechanism of nascent site deactivation, are provided elsewhere [17]. A prototypical example of the latter is desorption of CO from a graphene cluster $C_{25}H_{11}O_2$, subsequent to dissociative adsorption of O_2 on two free adjacent zigzag sites in a seven-ring cluster $C_{25}H_{11}$: the optimized cluster $C_{24}H_{11}O$ contains three unpaired electrons (M=4) and there is no ring closure at the nascent sites, whereas the deactivated cluster forms a five-member ring and its ground state is a doublet (M=2).

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