Spin State Splitting in Carbon Gasification Models

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Complete active space self-consistent field calculations have been performed on several models commonly used to investigate carbon gasification rates. These calculations clarify the level of electronic spin state splitting in these models. The spin splittings are much smaller than previously calculated, indicating that ab initio methods capable of describing, for example, open shell singlet states are required to perform accurate calculations on these models. The hybrid density functional theory methods commonly used to investigate gasification reactions do not fulfill this criterion.

1. Introduction

The gasification of carbons by oxygen-containing species is a vital process in the combustion of coal, making it a central process in the world's economy since the industrial revolution. The gasification process is challenging to describe in its entirety, being dependent on a wide range of surface structures and functional groups. Gross details, such as the fact that reactions on the edges of the graphitic structures of carbon chars dominate the gasification process, are well-known.[1] Further, making sense of the details of the bulk gasification process can be aided by microscopic modeling of representative reactions on carbonaceous surfaces.

Electronic structure theory calculations of the energetics of gasification reactions have been performed since the 1980s. Yang and co-workers were early pioneers, performing calculations on graphitic models with functionalized and unsaturated edge carbons. These early calculations start with rather qualitative semiempirical approaches[2−5] before moving on to more sophisticated Hartree−Fock and B3LYP levels of theory.[6,7] These calculations lead Chen and Yang to propose their "unified mechanism" of carbon gasification.[8]

Montoya et al.[9] make a significant addition to the ab initio modeling of carbon gasification processes by investigating different spin states in the model clusters. These results demonstrate that the models used for gasification reactions can have low-lying excited states or degenerate ground states. Furthermore, these results imply that the spin state that is the ground state in the model reactant does not necessarily correspond to the state exhibiting the lowest-energy minimum energy path for the gasification process being modeled. Thus, nonadiabatic reaction rate theories that take into account intersystem crossing may be required. To date, only simple transition state theories have been applied.

Montoya and co-workers had previously[10] established that for a number of zigzag edge graphenes the B3LYP method suffered less from spin contamination than the Hartree−Fock level of theory, and so used the hybrid B3LYP in their study of spin state energetics. Frankcombe and Smith[11] argue that the level of spin contamination in unrestricted B3LYP calculations along gasification pathways is still unacceptably high in Montoya's five ring model. Restricted B3LYP calculations suggest a much higher singlet−triplet splitting than that found by Montoya et al. Frankcombe and Smith also demonstrate a previously unconsidered low energy gasification mechanism, where the desorbing CO fragment migrates first to a "surface complex" before dissociating to the gas phase.

In turn, Sendt and Haynes[12] point out that the restricted methodology that leads to singlet−triplet splittings of the order of hundreds of kJ/mol corresponds to an excited singlet state in which electrons are forced to be paired. Using unrestricted B3LYP calculations, Sendt and Haynes find a small splitting between the lowest energy spin state and the next lowest energy spin state (of the order of 10 kJ/mol or less) in a range of molecules relevant as carbon gasification models.

All of these calculations, and a number of recent calculations on similar systems,[13−18] use methods that are known to have deficiencies for the types of systems being studied. The model systems with unsaturated carbon edge sites form biradical species, with weakly interacting unpaired electrons on different carbon centers. It is well-known that unrestricted DFT and hybrid calculations can give poor results for biradical systems,[19−23] usually giving spuriously large spin state splittings even in cases where the structures and spin state orderings are determined reasonably. This is alluded to by Sendt and Haynes.[12,18] Indeed, in ref 18, these authors recognize that the spin state splittings they calculate are likely incorrect and treat the kinetics of their model systems as though the lowest spin states have zero energetic splittings.

The aim of this work is to clarify the magnitude of the splitting between the ground state and next lowest spin state in a number of unsaturated carbon structures used in gasification modeling. To that end, multiconfiguration ab initio methods were applied to the model systems for a number of spin states.

Note that throughout this work it is assumed that kinetic theory calculations on model graphene systems aim to determine the exact rate of reaction for the model. How the rate of this restricted model should be interpreted in terms of macroscopic carbon gasification processes is not addressed.

Only reactant states have been investigated in this work. That is, transition state regions have not been studied. To the author's knowledge, a rigorous assessment of the accuracy of (hybrid) DFT calculations of the energetics in bond-breaking regions for carbon gasification modeling is absent from the literature, despite the huge effect any inaccuracies have on calculated rate constants.

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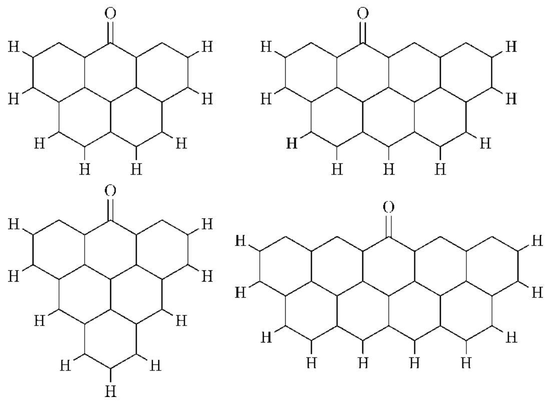

Figure 1. Carbon gasification precursor models used in this work. Top to bottom, left to right: five, six, seven, and nine ring models. Aromatic structure is not explicitly shown.

2. Method

Four graphitic gasification precursor models were investigated in this work. These models are the same or similar to those used previously[5,7,9,12−16,24] and are intended to describe gasification of the zigzag edge of a graphitic solid. Illustrated in Figure 1, these structures ranged from five to nine carbon rings. One zigzag edge of each was left unsaturated, while all other edge sites were capped with hydrogen atoms. A single oxygen adatom was present on the exposed zigzag edge in a ketone or semiquinone structure. For modeling the gasification process, this oxygen atom and the carbon atom to which it is bonded would be removed to form CO, either directly or via a surface complex.[11]

All electronic structure calculations were performed using Molpro 2006.1.[25,26] Self-consistent field (SCF) calculations were performed to generate an initial set of orbitals. After examination of the SCF orbitals and possible exchange of orbitals to bring the desired orbitals into the frontier set, complete active space SCF (CASSCF) calculations[27,28] were performed to calculate the required energies and forces. After initial explorations with restricted and unrestricted Hartree−Fock SCF orbitals, all reported calculations were performed using the restricted, open-shell Hartree−Fock (ROHF) orbitals from a high-spin calculation (all radical electrons unpaired) as the CASSCF initial orbitals. This approach consistently gave the lowest or equal lowest CASSCF energies, presumably through a more balanced description of the relevant orbitals than the equivalent unrestricted Hartree−Fock orbitals.

Unless otherwise noted, all energies quoted in this work are for structures after complete geometry optimization. Also unless otherwise noted, the minimum active space of n electrons in n orbitals [CASSCF(n,n)] was used for the model with n radical electrons. (Note that such an active space contains all of the configurations required to describe all spin states up to and including the fully unpaired state.) Point group symmetry was not imposed on the geometries or wave functions.

3. Results

For the five, seven, and nine ring models, the unpaired edge electron states clearly have two, three, and four unpaired electrons, yielding the triplet, quartet, and quintet states as the high-spin state, respectively. As a neutral molecule, the six ring model has an odd number of electrons. Thus, in that case, the appropriate spin state for unpaired electrons on the two unsaturated carbon atoms was the quartet state. In the ROHF solution, the third unpaired electron occupied an orbital composed of out-of-plane p atomic orbitals, mostly from the carbon atoms far from the unsaturated zigzag edge of the model.

TABLE 1: CASSCF(n,n) Energies of Precursor Models Relative to the Lowest Energy Spin State Energy (kJ/mol)

model	n	spin state	energy
five ring	2	singlet	0.051
		triplet	0
six ring	3	doublet	1.801
		quartet	0
six ring cation[a]	3	doublet	0.048
		quartet	0
seven ring	3	doublet	0.043
		quartet	0
nine ring	4	singlet	0.043
		triplet	0.031
		quintet	0

[a] At the geometry of the neutral.

For the five ring model, the two singly occupied orbitals in the ROHF triplet wave function corresponded to the required unpaired electrons on the unsaturated edge atoms. Likewise, for the six ring model, two of the three singly occupied ROHF orbitals corresponded to the desired unpaired electrons on the unsaturated carbon sites. However, for the seven and nine ring models, in the ROHF solution one or more of the orbitals that would describe an unpaired electron on an unsaturated edge atom was not one of the n highest energy occupied orbitals. In these cases, the required orbitals had to be rotated into the active space prior to the CASSCF calculation. The energy ordering of the orbitals around the frontier region was strongly dependent on the geometry used for the ROHF calculation.

The calculated CASSCF energies are give in Table 1. In all cases, the high-spin state was the lowest energy state. In the five, seven, and nine ring models, the spin state splitting was very small. The six ring model was found to have a substantially larger splitting than the other models, at nearly 2 kJ/mol. All of these splittings are significantly smaller than any previously published splittings for these models.[9,11,12]

Of the models considered in this work, the six ring model was unique in having an odd number of electrons. The active space used was necessarily comprised not only of the unpaired electrons on the unsaturated carbon atoms, but also the remaining odd electron that occupied a delocalized π molecular orbital. It is then reasonable to speculate that the spin state splitting being 2 orders of magnitude larger in the six ring model than in the other three models was due to including this third electron and orbital in the active space. As this third orbital exhibited antisymmetry with respect to the perpendicular plane bisecting the model, this orbital contributed unequally to the states with parallel or antiparallel electron spins in the other two orbitals. This hypothesis was confirmed by calculating the splitting between the singlet and triplet states of the cation of the six ring model at a single geometry, which was found to be small. No attempt was made to calculate the solution that arises by excluding excitations to and from the third, nonedge radical orbital.

As mentioned above, the n,n active space leading to the energies of Table 1 is the minimum active space required to describe the desired states. Active spaces containing up to 10 electrons and up to three virtual orbitals for the high-spin state were tested. Increasing the size of the active space did make a substantial difference to the CASSCF energies. However, this change in the calculated energies was a result of improving the description of the delocalized π system, applying equally to both

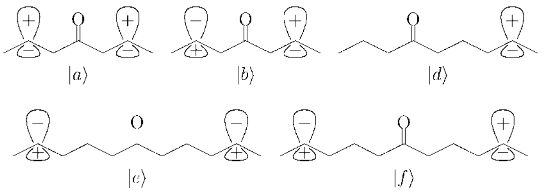

Figure 2. Schematic representation of the orbitals contributing to the low-spin CASSCF wave functions. $|a\rangle$ and $|b\rangle$ were present in all models. The third (π) orbital of the six ring model, denoted $|c\rangle$, is not shown. $|d\rangle$ was present in the seven ring model only. $|e\rangle$ and $|f\rangle$ were present in the nine ring model only. See also Table 2.

TABLE 2: Unnormalized Approximate Wave Functions for Low-Spin States, Built from Orbitals Shown in Figure 2

model	state	wave function
five ring	singlet	$a^2b^0 - a^0b^2$
six ring	doublet	$a^2b^0c^\alpha - a^0b^2c^\alpha$
seven ring	doublet	$3a^2b^0d^\alpha - 3a^0b^2d^\alpha + a^\beta b^\alpha d^\alpha + a^\alpha b^\beta d^\alpha - 2a^\alpha b^\alpha d^\beta$
nine ring	triplet	$a^\alpha b^\alpha e^2f^0 - a^\alpha b^\alpha e^0f^2 - a^2b^0e^\alpha f^\alpha + a^0b^2e^\alpha f^\alpha$
	singlet	$3a^2b^0e^2f^0 - 3a^2b^0e^0f^2 - 3a^0b^2e^2f^0 + 3a^0b^2e^0f^2$ $-a^\alpha b^\beta e^\alpha f^\beta - a^\beta b^\alpha e^\beta f^\alpha - a^\alpha b^\beta e^\beta f^\alpha - a^\beta b^\alpha e^\alpha f^\beta$ $+2a^\alpha b^\alpha e^\beta f^\beta + 2a^\beta b^\beta e^\alpha f^\alpha$

the singlet and the triplet states. The singlet−triplet splitting remained 0.05 kJ/mol.

Generally, the energies quoted in Table 1 are for completely relaxed structures in each state. The relaxed geometries for each spin state were indistinguishable. Vertical excitations (determined by calculating the lower spin state energies at the geometry optimized for the lowest energy state) resulted in nearly identical splittings, except for the neutral six ring model for which the vertical excitation energy was 0.02 kJ/mol higher. Likewise, singlet−triplet state averaged CASSCF calculations for the five ring model yielded identical results. These results are consistent with weak interactions between the radical centers, giving rise to the small spin state splitting calculated in this work.

CASSCF calculations give much more than simply the energies of the various states. Physically relevant representations of the electronic wave functions are also available, in terms of the CASSCF orbitals and CI vectors. These are indicated in Figure 2, which gives a schematic representation of the orbitals constructed within the n,n active space, and Table 2, which gives unnormalized approximate wave functions in terms of configuration state functions (CSFs) constructed from the orbitals of Figure 2. In Table 2, an x^2 means orbital x was doubly occupied in the CSF, x^0 means orbital x was unoccupied in the CSF, while x^α and x^β indicate an orbital singly occupied with a spin up or spin down electron, respectively. The expressions in Table 2 include all CSFs with normalized expansion coefficients greater than 0.05.

For the five and six ring models, Figure 2 and Table 2 can easily be interpreted as an open shell singlet (OSS) on the unsaturated edge. For the six ring model, an independent doublet was also present, as expected. For the seven and nine ring models, contributions from CSFs with all electrons unpaired made the interpretation of the wave functions less obvious, but the same conclusions could be drawn. For the seven ring model, the doublet CASSCF wave function was primarily a combination of an OSS with a doublet primarily from an unpaired electron on the unsaturated carbon atom furthest from the oxygen adatom. For the nine ring model, the wave functions were primarily constructed from OSSs on pairs of equivalent unsaturated carbon atoms.

4. Summary and Conclusion

Spin state splittings have previously been given for the five and six ring models.[9,11,12] However, due to the inappropriate use of single configuration levels of theory, the published splittings are too large. These models are best described as independent radical centers (such as a biradical in the two unsaturated carbon cases) with the accompanying very small spin state splittings. Single configuration electronic structure theory methods such as the B3LYP method cannot reliably describe these systems.

With the exception of the neutral six ring model, all calculations performed in this work indicated a spin splitting around 0.05 kJ/mol. The larger splitting found for the six ring model, still much smaller than that available in the literature, could readily be explained by asymmetric interactions with the distributed π radical.

All other things being equal, a spin splitting of 0.05 kJ/mol yields a thermal upper state population [determined from the Boltzmann factors $\exp(-\Delta E/kT)$] of 98.0% of that of the ground state at 300 K. At temperatures more relevant to combustion modeling, the populations are even closer, with the upper state population being 99.3% of the ground-state population at 800 K. Thus, the approach of Sendt and Haynes[18] of effectively setting the splitting to zero is justified. This effect alone can change calculated gasification reaction rates by a factor of up to 4, depending on the degeneracies of the spin states involved.

Clearly, how these electronic states behave during the gasification reactions will strongly affect how kinetic theories should be applied to the models. If the spin splitting in the vicinity of a reactive saddle point is calculated to be much larger than it really is, a single-surface rate theory may be applied when inappropriate. Even worse, if the energy ordering of spin states is calculated incorrectly in the vicinity of kinetically relevant saddle points, kinetic theories can be applied on the wrong potential energy surface, resulting in calculated model reaction rates in error by many orders of magnitude. Such errors are potentially far more severe than the already substantial risk of determining barrier heights with insufficient accuracy due to inherent deficiencies in the electronic structure theory applied.

It is worth pointing out that the reaction path calculations of the type that are susceptible to errors due to incorrect assessment of spin state splittings[9,11−13,16−18] are not the only way to derive rates for microscopic processes involved in gasification. Approaches that build models based on bond energy calculations and fit these to experimental kinetic measurements, such as the work of Chen and Yang,[8] are not directly affected by the considerations of the current work. However, the likely population of available spin states requires careful consideration if one wants to draw firm conclusions about the rates of microscopic processes from these phenomenological fits.

Appropriate active spaces to give a continuous description of the electronic states along the reaction paths have not yet been determined.

It remains to be pointed out that when applying transition state theories to carbon gasification reactions, it seems reasonable to consider all possible spin states arising from the unpaired electrons on unsaturated edge carbon atoms as being degenerate. While the fate of these spin states in the bond breaking regions remains largely unknown, the bonding rearrangements among the edge carbon atoms upon CO dissociation suggest that states arising from unpaired electrons near the desorption site will split in the transition state region. This means that populations of different spin states need only be considered for determining reactant partition functions and that spin state population effects do not cancel between the reactant and transition state partition functions.

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Supporting Information Available: Illustrations of the occupied correlated CASSCF natural orbitals for the graphene−oxygen species considered in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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