PROGRESS TOWARD CALCULATION OF CARBON GASIFICATION THERMAL RATE CONSTANTS

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Introduction

The gasification of carbonaceous materials is an extremely important process in many applications. As such, there have been many efforts to computationally model the gasification over the past four or five decades. The simplest models assume that the oxidation of the carbon atoms occur on the surface of shrinking solid particles. More complex models take into account reaction on the walls of pores and the growth and evolution of the surface pore structure. More sophisticated still are the models reflecting the observed structure of coal chars—small graphitic layers irregularly stacked into crystallites. Good summaries of the existent models are given in Bhatia and Gupta[1] and Bhatia[2].

The emergence of models, which involve the microscopic details of the coal char, has raised the importance of understanding the microscopic gasification processes. While developments such as Yang's *unified mechanism* for carbon gasification reactions[3] offer insight into the microscopic processes at work during gasification, the opportunity to more directly investigate the properties of the microscopic processes and calculate dynamic quantities such as rate constants is offered by molecular orbital theory.

Advanced molecular orbital theory has been used by several authors to investigate these reactions since the pioneering 1998 work of Chen and Yang[4,5] which seems to have fixed a standard methodology for the investigation of these reactions. Montoya *et al.*[6] made the important contribution that overcoming spin contamination is vital in obtaining accurate energies for graphenes, and that the B3LYP formulation does not suffer from excessive spin contamination.

Despite this attention, little progress has been made in elucidating reaction paths with sufficient detail to directly calculate rates of the various microscopic processes in order to compliment or validate gasification modelling. This study presents progress toward that goal.

Methodology

The main gasification reaction of interest in this work is the extraction of a carbon monoxide fragment from an initial state of a graphene with an oxygen atom chemisorbed onto a carbon atom in an exposed "zig-zag" edge site. The enthalpy change for the reaction is easily calculated from the energies (corrected for thermal effects) of the optimized initial state (graphene with chemisorbed oxygen) and the product state (graphene with CO removed plus the CO fragment). The B3LYP hybrid method was used as a compromise between accuracy and tractability. Calculations have been performed using the 3-21G, 3-21+G(d) and 6-31G(d) basis sets.

Essential for the application of transition state theory is the identification of the transition state (TS) for a reaction. For many reactions occurring over a reaction barrier the TS is the geometry corresponding to the highest energy along the minimum energy pathway (MEP), and this serves as a useful first approximation. Hence a major focus of this work is in identifying these saddle point TSs.

A useful way of searching out a MEP with molecular orbital theory calculations without explicitly integrating energy gradients involves first identifying a parameter of the geometry specification likely to be a reasonable reaction coordinate for the reaction of interest. This coordinate can then be frozen at successively longer values (or shorter values for association reactions) and the remaining coordinates optimized. This manual stepping of the likely reaction coordinate allows the MEP to be followed at an arbitrary level of detail and can easily find unexpected changes in the MEP, particularly if symmetry constraints are relaxed.

Results

The main graphene used in this work has been a $C_{19}H_8$ molecule similar to that used in previous investigations. The carbon structure is arranged into five aromatic rings, as shown in figure 1. One side of the carbon structure is left exposed to simulate the reactive edge sites during gasification while the other edges are capped with hydrogen atoms in order to minimize truncation effects. In all the calculations reported here spin contamination was acceptably low, with the calculated $\langle S^2 \rangle$ differing from the exact $S(S+1)$ value by around 0.01%.

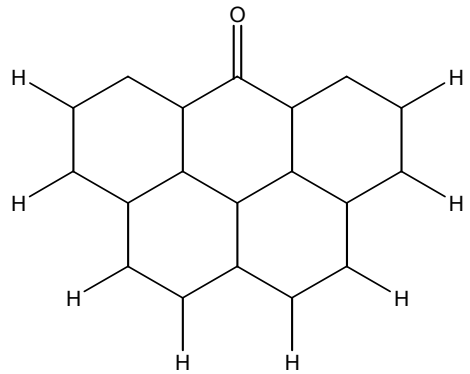

Figure 1. Model $C_{19}H_8$ graphene with oxygen atom chemisorbed onto the central bare zig-zag site

The ground state of the reactant state (after adding an oxygen atom to the central bare carbon site to make $C_{19}H_8O$) is the triplet state. However the potential minimum for the reactant in the singlet state is almost degenerate with the triplet, being calculated to be 0.18 kJ/mol higher in energy with the 3-21G and 3-21+G(d) basis sets and 0.076 kJ/mol higher in energy with the 6-31G(d) basis set. As has been pointed out by others[7] this near degeneracy implies that both the singlet and triplet states need to be investigated as the singlet state will be significantly populated.

Straight gasification. The gasification reaction is assumed to take the CO fragment and pull it directly out of the graphene. A rather substantial complication of following this reaction path is that when all symmetry constraints are removed the actual MEP brings the CO fragment out of the plane of the remaining graphene to a position above the center of the remaining five atoms from the broken C_6 ring. The extent of the movement out of the plane is clearly an artifact of the single plane model being used as neighboring carbon planes in a real graphene would either prevent such motion or recapture the CO fragment. To counter this the geometry has been artificially restricted to C_{2v} or C_s symmetry, maintaining the CO fragment in the plane of the graphene. To follow the restricted MEP the reaction coordinate used was one of the Cartesian coordinates of the extracted carbon atom after aligning the graphene with the Cartesian axes: this single carbon atom coordinate is in effect the perpendicular distance between the extracted carbon atom and the remaining exposed edge. All other coordinates, including the position of the CO fragment relative to the broken C_6

ring, were allowed to relax. It was possible to freeze selected other coordinates to allow grid scanning of the potential.

For the triplet state, the MEP *does not* maintain the C_{2v} symmetry that other studies have suggested. C_{2v} symmetry is maintained as the CO fragment is moved the first 0.7 Å from its potential minimum position. Between 0.7 Å and 0.8 Å the potential well the CO fragment was following flattens and the fragment spills into an adjacent well. Following the adjacent, C_s symmetry well downhill leads back into the C_{2v} symmetry well. Extracting the CO fragment in a similar way on the singlet surface maintains C_{2v} symmetry throughout.

The singlet and triplet TSs are significantly different. While the triplet TS of C_s symmetry presents an energy barrier to reaction of around 500 kJ/mol, the singlet C_{2v} TS occurs at much lower energies, around 380 kJ/mol above the reactant state.

There are significant basis set effects on the calculated potential energy surfaces for both the singlet and triplet states. In the region of the triplet TS the three basis sets used produced significantly different energies, with the inclusion of diffuse functions in the 3-21+G(d) basis (generally required to accurately model such long-range, bond breaking processes) apparently responsible for the increase of the energy in the region of the TS by around 30 kJ/mol. In the singlet case the position of the TS (as measured by the distance of the extracted carbon atom from its reactant state position) changes from 1.10 Å for the 3-21G basis to 0.81 Å for the 6-31G(d) basis.

Multi-step mechanisms. While the direct gasification path is the most obvious, even in the small five-ring model being used here other paths exist. Fixing and stepping the Cartesian coordinate that moves the CO fragment across the exposed edge in a similar way to the direct extraction coordinate reveals that on the triplet surface, motion across the face quickly requires in excess of 500 kJ/mol of energy. However on the singlet surface such motion offers a viable alternate reaction path—possibly even a preferred path. Breaking one carbon-carbon bond and migrating the CO fragment to a carbonyl structure attached to an adjacent zig-zag site passes through a TS significantly lower in energy than the direct gasification barrier, being around 280 kJ/mol above the potential minimum. The migrated carbonyl structure is a stable species 90 kJ/mol above the potential minimum. Chen and Yang[5] suggest that carbonyl should be significantly easier to gasify than the direct extraction, meaning that this may be an energetically preferred path.

Conclusion

This work supports the notion[7] that while the ground state of the $C_{19}H_8O$ model molecule is technically a triplet, the very small energy gap to the singlet state and the availability of significantly lower energy reaction pathways on the singlet surface suggests that it is the singlet state that will be react. The near degeneracy of the singlet and triplet states will introduce a factor of two modification into the rate constants eventually calculated for the reaction on the singlet surface.

Basis set effects are very strong in the reasonably small basis sets used here. Adding diffuse functions seem to have a strong effect on the energy in the region of the TS. The position of the highest energy point along the calculated singlet MEP is changed by 30% with the move from the 3-21G basis to the 6-31G(d) basis.

The migration of the CO fragment onto adjacent edge sites has been examined here for the first time and is likely to compete effectively with direct gasification. While dynamical considerations will likely decide which process ultimately facilitates gasification, the existence of paths such as these need to be investigated further. Inter-plane interactions are likely to be important. The out-of-plane nature of the true TS for the single plane model examined here means that multi-plane models must be investigated to successfully model bulk char edge reactions. Progress towards multi-plane models continues.

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