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MODELING MERCURY SPECIATION IN COAL COMBUSTION SYSTEMS AND INTERACTIONS ON ACTIVATED CARBON

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Project Description

The control of mercury emissions is a major concern in coal-fired power industries. Many approaches have been used to date to capture at least some of the mercury emitted in the flue gas streams of coal-fired power plants, amongst which is the injection of powdered activated carbon into the gas stream. The mechanisms of mercury interactions with activated carbon (AC), however, are complex and rarely understood, and as a result, there is considerable research interest on this subject. The EERC has recently developed a model (1) based on extensive experimentation that gives more details about the nature of interactions of mercury with AC and the flue gas components. However, the complexity of the mercury reactions with flue gas components and AC surface makes it difficult to obtain quantitative measurements for reaction rates, rate constants, and thermodynamic stabilities of reactants, intermediates, transition states, and products.

This project, therefore, was focused on using a theoretical approach to evaluate the Hg interactions with carbon by the proposed zigzag and armchair carbon graphene-edge structures. Quantum mechanical calculations can provide information about thermodynamic stabilities and kinetic constants for the proposed intermediates and their conversions. Also, the calculations involving interaction of the proposed carbenium ion intermediates with elemental mercury yields useful information on the oxidation of mercury on the carbon surface or the role of AC in the oxidation process.

This study was divided into two main tasks, and the calculations were performed on a Sun Fire V1280 Server using the Gaussian03 (2) program suite. The first task involved an assessment of theoretical electronic structure methods against G3 theory (3) in the quest for a computationally intensive ab initio method to use for these calculations, while the second task involved the use of the chosen method to characterize all possible reactants, intermediates, transition states, and products of all elementary reactions in the proposed model.

Goal

The main goal of this project was to use a computational approach to develop the mercury–flue gas carbon theory on a quantitative basis using the more complex structural or mechanistic model that the

EERC has recently developed (1). The predicted structural and/or system condition modifications could lead to improved sorbent technologies. The specific objectives were:

- To determine energy minima on the potential energy surfaces (PESs) of the important structures.
- To derive thermodynamic data that lead to the calculation of rates and rate constants.

Rationale

The rationale for this research derives from the desire to reduce the levels of mercury emissions in industrial flue gas streams. Power industry and coal companies in particular, can use this model to evaluate and/or improve their fuel performance, energy production capacities, and mercury emission control options. The baseline case of this model should provide power plants with information on the optimum conditions for efficient mercury capture in gas stacks using injected AC.

Approach

The project was carried out entirely by performing quantum mechanical calculations based on the structural mechanism that was recently proposed. The software package used in these calculations was the Gaussian03 (2) suite of programs, which was recently installed on a Sun Fire V1280 server at the EERC. The theoretical method used was MPW3LYP (4), which is a hybrid density functional (DFT) method for thermochemistry. A combination of basis sets including the 6-311+G** (5–9) and Stuttgart 1997 (7–9) were employed for the organic moiety and mercury atom, respectively.

Computational Model

According to the proposed model for the interactions of Hg on AC zigzag edge surface, the following reaction sequence was envisioned:



where R = H, CH₃, Ph and combinations. A total of six molecules were generated as shown in Figure 1a–f. The desired molecule that was used to represent a carbon zigzag-edge structure, phenalenylidene, is shown in Figure 2.

The rate constants are calculated using the following equation of the transition states theory:

$$k_{rxn} = \frac{k_b T}{h} \frac{q_{ist}}{q_A q_B} e^{\frac{-E_a}{k_b T}} \quad [4]$$

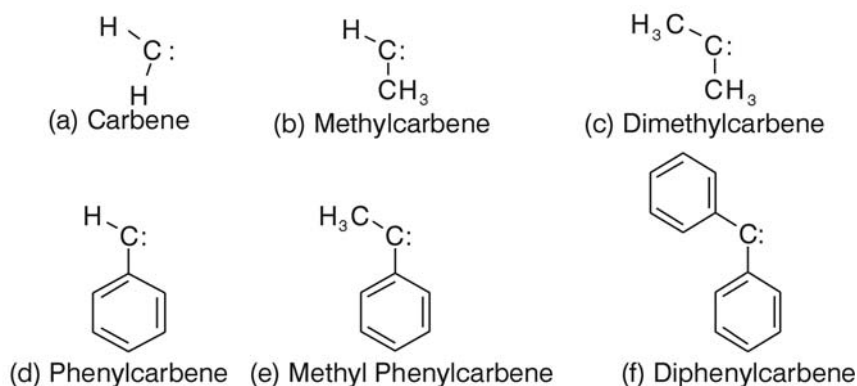


Figure 1. Simple prototype structures used in assessing the optimum theory level.

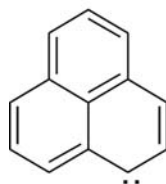


Figure 2. Phenalenylidene (g).

where k_b is the Boltzmann's constant, h is Plank's constant, q_{tst} is the partition function of the transition state, q_A and q_B are the partition functions of the reactants, E_a is the activation energy, and T is the temperature in Kelvin.

Progress

Several equilibrium structures (about 42 molecules) have been optimized at the MPW3LYP (4) level of theory. The minima of all the structures, reactants, intermediates, and products generated from the prototypes shown in Figure 1a–f and Figure 2 involving elementary reactions shown in Equations 1–3 have been obtained on their PESs. Theoretical harmonic vibrational frequencies have also been calculated, and all of these molecules were shown to be true stationary points on their respective PESs by the absence of imaginary frequencies. Trends in free energy changes (ΔG), enthalpy changes (ΔH), and reaction energies (ΔE) for all the elementary reactions are shown in Figures 3–5. A guide to interpreting the trends in the figures is that the more negative the energy, the more favorable the process. In general, Figure 3 shows that proton attachment is progressively favorable on going from small molecules to the more complex carbon-edge structures in the gaseous phase at 298.15 K. On the other hand, the insertion of Hg(0) (Figure 4) on the surface is less favored with increasing molecular size toward a graphene-edge structure at the same temperature. The capture of Cl⁻ is shown in Figure 5, and it is a feasible process at

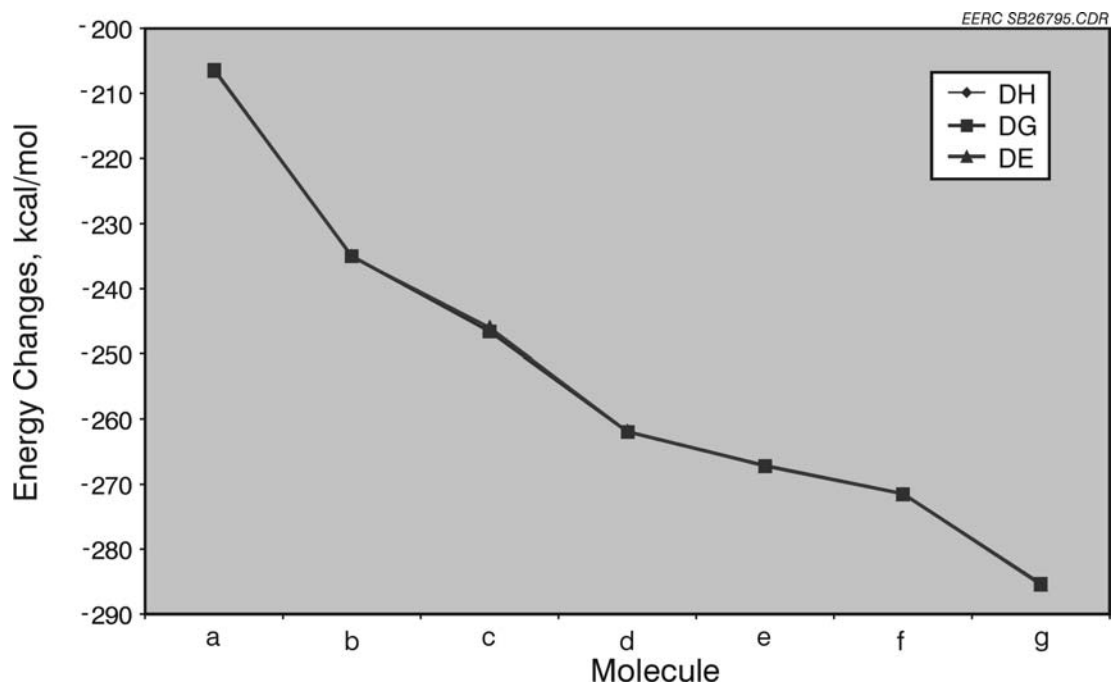


Figure 3. Trends in free energy changes (ΔG).

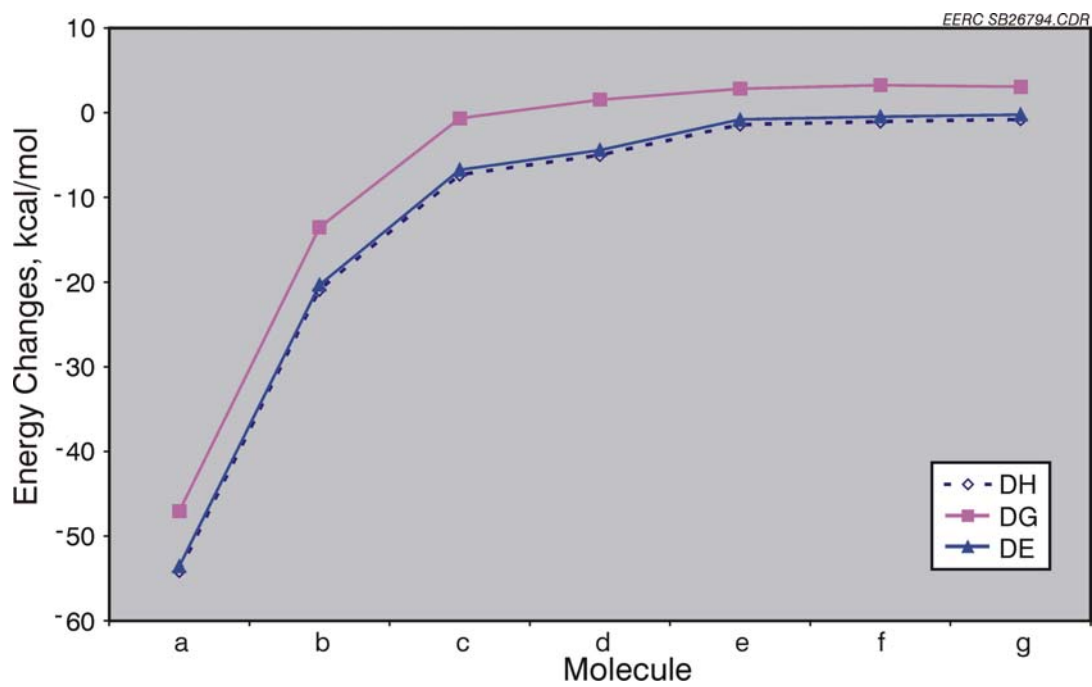


Figure 4. Enthalpy changes (ΔH).

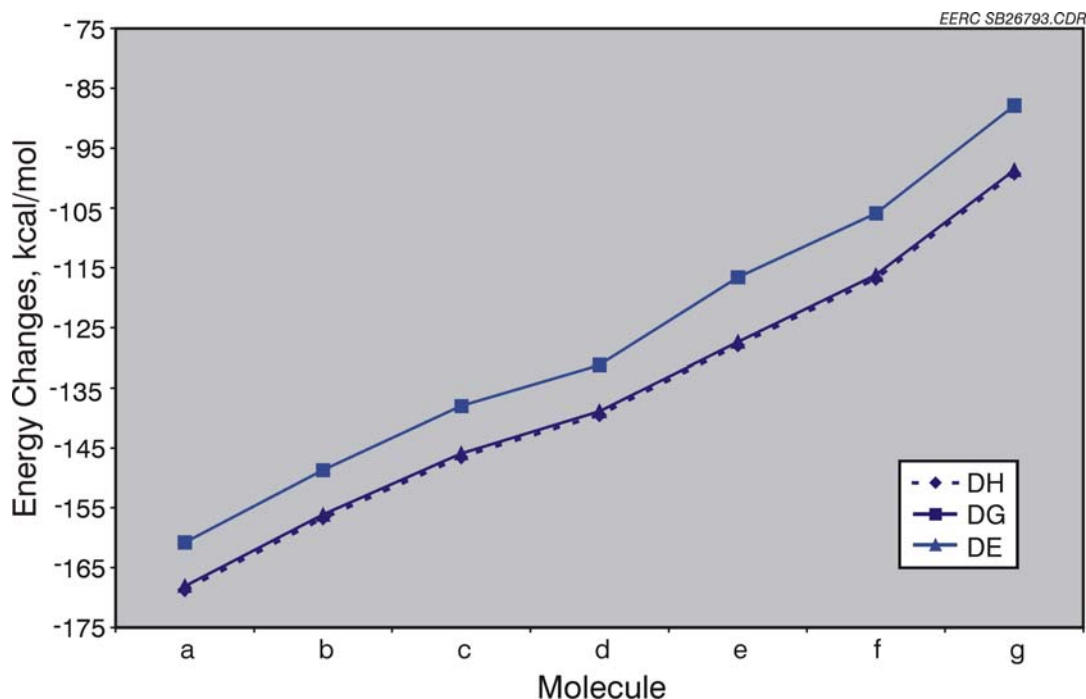


Figure 5. Reaction energies (ΔE).

298.15 K although with a decreasing tendency toward graphene-edge structures as the energy change slowly rises but not becoming positive.

In order to investigate the rates of these elementary reactions, all the transition states involved in the elementary steps need to be characterized. From these calculations, the energy of activation E_a (barrier height), enthalpy of activation ΔH^\ddagger , and free energy of activation ΔG^\ddagger can be obtained for these elementary reaction steps. Barrier height estimates allow one to be able to estimate the rate constants using the transition states theory approximation. These calculations are ongoing and have been slowed down because of some problems with the Gaussian03, which have to do with a limitation of some algorithms in the software.

Quality Assurance/Quality Control

Quality Objectives

The quality objective of this project is to obtain quantitative thermodynamic data and rate constants that will further validate the developed mechanistic model or provide information that could lead to the adjustment of certain experimental parameters in the most cost-effective manner.

Measurement/Data Acquisition

The computational model was based on the experimentally proposed one, which was made up of a structural mechanism that offered the possibility to perform computations of the energy minima on the reactants, intermediates, and products. These calculations were carried out using the Gaussian03 (2) software package recently installed on a Sun Fire V1280 at the EERC.

Assessment and Validation

The theoretical method used in these calculations was chosen based on an assessment against the G3 theory (3) that is known to produce accurate thermochemical data but requires prohibitively high computer resources to perform calculations on large molecules such as the prototype in Figure 2.

Status

The project is about 85% to 90% complete. Most of the energy minima have been obtained using the MPW3LYP hybrid density functional theory method that was chosen based on the assessment study. Thermochemical data including reaction energies, enthalpies, and free energies have been derived from these calculations. This information is already offering some ideas as to the role of AC in the interactions of Hg with flue gas components at room temperature in the gas phase. The remaining part of the work is to finish calculations of the transition states in order to calculate rates and rate constants. This last part of the project has been slowed down seriously because of a limitation in one of the algorithms in Gaussian03 that is used for calculations of transition states and also partly because the proposed molecules are large. In order to circumvent this problem, a combination of approaches is being adopted, and this requires more time for one calculation. In this project, the focus was on the chloride ion as the halogen atom but the study could be extended to investigate the effects of other halogens. It is also possible to consider a substituted graphene surface and investigate how this could affect the Hg interactions with other flue gas components.

Potential Applications and Benefits

The results from this study are expected to be valuable to the power industry and coal companies. Efficient Hg-capturing technology will not only allow these companies to scale their energy production capacity but also enable them meet with state and federal Hg emission regulations. Economically, optimizing the conditions for Hg capture via the use of injected AC makes the technology cost-effective while achieving the same goals. A direct benefit from meeting emission standards is a reduction in health hazards related to atmospheric and/or environmental mercury exposure.

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