Elementary reaction pathways leading to oxidation of soot by hydroxyl radicals (OH) were explored theoretically. Three prototype reaction systems were chosen and their energetics were computed employing a density functional theory. The first two, benzene + OH and a benzene-phenol complex, did not result in pathways leading to CO expulsion. The third reaction system, OH attacking a phenanthrene radical, had multiple pathways leading to CO elimination. This reaction was composed of four different oxyradical decomposition pathways connected by H atom migration.

1 Introduction

Formation of soot comprises a number of sequential steps, including soot precursor formation, particle nucleation, and particle coagulation. Parallel to these sequential steps are surface reactions taking place on the edge of both polycyclic aromatic hydrocarbons (PAH) and soot (Frenklach 2002). Surface reactions include the addition and removal of carbon. In this study we continue our exploration of surface oxidation reactions.

Previously, we focused on decomposition of oxyradicals, presumably key intermediates in the oxidation pathways. In pursuit of that objective, we determined reaction rates for the thermal decomposition of oxyradicals located on the zigzag (You et al., 2011) and armchair (Edwards et al., 2013) PAH edge sites. Oxidation of aromatic radicals by O\(_2\) (Tokmakov et al., 2005; Zhou et al., 2012) has also been studied. To our knowledge, no atomistically resolved pathways leading to the removal of carbon by OH have been identified.

Current models of soot formation typically describe oxidation by OH through collision efficiency, \(\eta_{OH}\) (Appel et al., 2000; Bisetti et al., 2012), assigning to it a value of 0.13, the lower bound determined for \(\eta_{OH}\) in the experimental study of Neoh et al. (Neoh et al., 1981). In their experiments, Neoh et al. examined the oxidation of soot in a two-stage atmospheric pressure premixed system. Soot was formed in the first burner under rich conditions, and then oxidized in
the secondary burner over slightly lean to slightly rich conditions. OH was found to be the principal oxidant of soot under these conditions. They reported $\eta_{OH}$ values in the range of 0.13–0.28.

Roth and co-workers performed shock tube experiments to study soot oxidation. They derived collision efficiencies for NO and O (Von Gersum and Roth 1992; Vierbaum and Roth 2002) as well as for OH and O$_2$ (Roth et al., 1991). $\eta_{OH} = 0.2$ was determined as a fitting parameter to account for the observed CO formation.

A study of Santoro and co-workers (Puri et al., 1994; Puri et al., 1995) reported lower bounds for $\eta_{OH}$, 0.04 for methane and 0.05 for methane/butane flames. These authors initially reported $\eta_{OH}$ to decrease with increasing temperature, but in a later communication (Puri et al., 1995) withdrew this conclusion. They also noted a trend of increasing $\eta_{OH}$ with time.

A series of experimental studies by Faeth and co-workers (Xu et al., 2003; Kim et al., 2004; Kim et al., 2008) examined the oxidation rates of soot over the ranges of 0.1–8 atm and 1400–2350 K in diffusion flames burning a variety of fuels. They concluded that $\eta_{OH}$, over all of their experimental conditions, was roughly constant at 0.12, with an uncertainty (95 % confidence) of ± 0.03 (Kim et al., 2008). Most of their data fall within this range, but some measurements were as low as 0.02 and as high as 0.4.

The purpose of the present study is to explore conceivable reactions of OH with PAH edges that may explain the experimentally observed $\eta_{OH}$ values. To this end, we computed potential energy surfaces (PES) of OH reacting with three types of PAH edge sites to explore possible pathways leading to CO expulsion.

2 Methods

Density functional theory (DFT) was employed to calculate potential energy surfaces of all stable species and transition states for the oxyradical systems. Geometry optimization and vibrational frequency calculations were performed to identify all stationary points on the reaction pathways using the B3LYP hybrid functional (Lee et al., 1988; Becke 1993) and a 6-311G(d,p) basis set (Krishnan et al., 1980). Zero-point energies and vibrational frequencies were scaled by a factor of 0.967 (Johnson 2005). Transition states were confirmed to connect the reactant and product species by inspection of the normal mode for the single imaginary frequency of each saddle point. All the quantum chemical calculations were carried out using the Gaussian 03 (Frisch et al., 2003) and the Gaussian 09 (Frisch et al., 2010) program packages.
3 Results and Discussion

3.1 Minimum energy paths

Three reactions were investigated as possible prototypes representing OH reacting with a soot surface. In doing so, the two fundamental soot surface sites, $C_{\text{surface}}\cdot\text{-H}$ and $C_{\text{surface}}\cdot$, were considered. In addition, the influence of interacting graphene layers on oxidation was also investigated. Of the three possibilities, pathways leading to CO expulsion were only found for OH attacking a $C_{\text{surface}}\cdot$ site. In this case, hydrogen migration was a key step that opened up the CO eliminating pathways. Below, we present the results from our investigation into the reaction of OH + $C_{\text{surface}}\cdot\text{-H}$, OH and layers, and OH + $C_{\text{surface}}\cdot$.

3.1.1 OH + $C_{\text{surface}}\cdot\text{-H}$

Benzene was used as a prototype for the $C_{\text{surface}}\cdot\text{-H}$ soot surface edge. The PES for this system, shown in Fig. 1, identified two main products, $\text{H}_2\text{O}$ (6) and phenol (9), with a third product (8) being essentially unreachable due to the high barrier that must be crossed. There were no pathways leading to CO expulsion. Recent theoretical studies of the same reaction (Tokmakov and Lin 2002; Hollman et al., 2011) also did not identify any channels leading to CO expulsion. We concluded, therefore, that OH reacting with a $C_{\text{surface}}\cdot\text{-H}$ edge of a graphene layer does not lead to CO expulsion.

![Figure 1. Potential energy surface for the reaction of benzene with OH at the B3LYP/6-311G(d,p) level of theory. Energies are in kcal/mol at 0 K relative to the reactants, 1.](image-url)
3.1.2 OH + Bi-layer

A benzene-phenol complex was used to model “interacting” layers of soot. After attaching to one layer, OH may react with another layer, providing a potential pathway for oxidation. The potential energy surface of this system was calculated with the M06-2X density functional (Zhao and Truhlar 2008) and 6-311G(d,p) basis set. B3LYP is unable to account for medium-range interactions (Zhao and Truhlar 2008), such as those in the benzene-phenol complex.

The computed PES is shown in Fig. 2. No pathways were identified for the removal of CO. Furthermore, the single transition state that was identified, TS 2-3, had a nearly 100 kcal/mol barrier, indicating that continuing along that pathway would not be feasible.

![Figure 2. Potential energy surface for the reaction of benzene with phenol at the M06-2X/6-311G(d,p) level of theory. Energies are in kcal/mol at 0 K relative to the reactants, 1.](image)

3.1.3 OH + C_{surface}

A phenanthrene radical was selected as the prototype for a C_{surface} soot surface site. The adduct and initial wells of the PES for the phenanthrene radical reacting with OH are shown in Fig. 3. The PES shows the formation of four oxyradicals: 8, 7, 5, and 6, associated with channels I, II, III, and IV, shown in Figs, 4(a)-(d), respectively. The formation of these oxyradicals is facilitated by the migration of H atoms. Each of these oxyradicals can continue to
isomerize down their respective pathways, eventually eliminating CO. The PES shown in Fig. 3 and 4 are on the singlet surface.

Pathways I-IV are oxyradical decompositions, similar in general features to those of the phenanthrene oxyradicals studied previously (Edwards et al., 2013). Each of these pathways, however, has distinctive reactions and varying barrier heights. For instance, PES I, III, and IV have similar transitions from oxyradical to cyclic intermediate. The barrier heights for these transitions are 15.3, 86.4, and 39.2 kcal/mol for PES I, III, and IV, respectively. In the previous study of armchair oxyradicals, the barrier height for the similar transition was 54.7 kcal/mol. This wide range of barrier heights is related to the location of a hydrogen atom with respect to the chemisorbed oxygen atom. In all of these cases, oxygen was located on the same site of the phenanthrene oxyradical. The relative location of the hydrogen atom and consequently the “ease” of its migration is the primary cause for all of the differences between the four oxyradicals observed in the present study.

Figure 3. Potential energy surface for the reaction of a phenanthrene radical with OH at the B3LYP/6-311G(d,p) level of theory. Energies are in kcal/mol at 0 K relative to the reactants, I. The roman numbers refer to corresponding PES in Fig. 4.
4 Conclusions

Oxidation of aromatic edge sites by OH was investigated. The energetics of three different graphene edge sites reacting with OH were computed in order to explore pathways leading to CO expulsion. Two reaction systems, OH + benzene and a benzene-phenol complex, did not exhibit pathways leading to CO expulsion. The third one, OH reacting with a phenanthrene radical on the singlet potential energy surface turned out to be the most promising of the three reaction systems studied, containing multiple pathways for CO elimination. Evaluation of reaction rates and their comparison to experiment is in progress.
Acknowledgements

DEE, WAL, and MF were supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division of the US Department of Energy, under Contract No. DE-AC03-76F00098. DYZ was supported by the National Science Foundation under grant NSF CHE-0809969. MF was supported by the US Army Corps of Engineers, Humphreys Engineering Center Support Activity, under Contract No. W912HQ-11-C-0035. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of the Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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