1 Introduction

The flow over hypersonic vehicles is characterized by extreme conditions with shock layer temperatures reaching 10,000 K and heat fluxes as high as 5 kW/cm². Thermal protection systems (TPS) consisting of carbon-based surface-ablating materials are effective structures that are able to heat flux to be carried away from the vehicle by the ablating material. At these high temperatures, dissociated oxygen atoms (O) strike the TPS surface leading to several possible gas-surface chemical reactions. Specifically, the oxygen atom could chemically bond to the surface, it could recombine with another adsorbed oxygen and leave the surface as a molecule (O₂), or the impinging atom could "oxidize" the surface creating products such as CO and CO₂ leaving the surface and being injected into the boundary layer. Such surface reaction results in the recession of the surface (surface ablation). Currently, much uncertainty exists in both the dominant reactions themselves as well as the rates of these reactions. The mechanisms and rates are required as input into large eddy simulations of hypersonic flows. Experimental determination of the chemical mechanisms themselves under extreme hypersonic conditions is difficult and often they must be inferred from macroscopic observations such as heat flux and surface recession measurements. However, this field of computational chemistry continues to evolve in step with advances in computational power; fundamental chemical studies may one day be able to provide insight into the chemical mechanisms and associated rates for such surface ablation processes.

The goal of this work is to develop finite rate models through large scale Molecular Dynamics (MD) simulations using the ReaxFF force field. Our current effort is to validate our ReaxFF simulations with existing data available from molecular beam experiments. In this work, we simulate the collision of hypersonic (5 eV) O atoms with graphitic materials including the removal of surface carbon atoms, the product species created, and the geometry of each product formed.

2 Molecular Dynamics Simulations

In contrast to previous computational chemistry work in this area where isolated single collision events are studied on graphite sheets (one atom layer), we simulate sequential gas-surface collisions on multi-layered graphitic (repeating HOPG) with large surface area. We do this to simulate the evolution of oxidized HOPG as observed on graphene sheets (one atomic layer), we simulate sequential gas-surface collisions on multi-layered graphene. The goal of this work is to develop finite rate models through large scale Molecular Dynamics (MD) simulations using the ReaxFF bond order dependent potential. Our current effort is to validate our ReaxFF simulations with existing data available from molecular beam experiments. In this work, we simulate the collision of hypersonic (5 eV) O atoms with Highly Oriented Pyrolitic Graphite (HOPG) and compare our results to the molecular beam experiments performed by Moton and co-workers.

2.1 ReaxFF Potential

ReaxFF is a bond order dependent potential that uses a relationship between bond distance and bond order along with the net removal of surface carbon atoms, the product species created, and the geometry of each product formed. Molecular Dynamics simulations are performed with the LAMMPS molecular dynamics program, using the ReaxFF potential.

2.2 Surface Preparation

The collision of a 5 eV O atom with the atomic-scale HOPG surface in each MD simulation results in a significant increase in the temperature of the simulated 'slab' of graphite. Under low pressure experimental conditions¹⁻³ any transfer of energy to the surface would be conducted into the bulk material long before the O atom is lost to the atmosphere. In our simulations we thermostate the bottom layer of the HOPG slab to maintain a constant surface temperature. However, in addition, we also had to wait roughly 12.5 ps before the increased temperature of the top layer cooled back to the thermostated surface temperature as shown in Figure 4. If the next gas phase atom is injected prior to this, it hits a surface at an artificially high surface temperature, not the ambient temperature of the experiment. Colliding atoms in 1 ps intervals without temperature control results in very high surface temperatures which cause the HOPG to erode much faster than it would in the experiment. However, simulating the system for 12.5 ps between collisions is computationally expensive and there are no reactions over this time scale. In fact, most reactions were observed to occur at short timescales (<1 ps).

2.4 Continuous Collisions

Oxygen atoms at 5 eV are continuously injected towards the HOPG surface. A total of 1000 continuous collisions were performed at 525 K. The simulation data predict the ratio of CO to CO₂ products as 1:2 while our simulations predict this ratio of products to be roughly 1.4. The fact that our simulations predict more CO than CO₂ and in a reasonable proportion compared to SDMS simulation is encouraging.

3 Conclusions and Future Work

In this work, we have studied the oxidation of HOPG by hypersonic O atoms. To avoid long wait times between successive collisions, we thermostated the system to the desired target temperature. It was also observed that the pristine HOPG sheet does not oxidize even by the collision of hyperthermal O atoms. However, a surface covered with oxygen groups and small intrinsic defects lead to oxidation of the surface. We created a surface coverage of 10% by allowing the O atoms to bond naturally to the surface instead of placing them in epitaxial form which results in bonding of the surface. Our simulations considered collisions at 373 K and found that the oxidation products were mainly CO and CO₂. This was consistent with the experimental observations. In our simulations, the predicted higher production of CO is consistent with the experimental data. However, the rate of production of CO is lower than that predicted by the experimental data. This may be due to the computational limitations of the simulation technique.

4 References