

OH Radical Oxidation of Ethylene Adsorbed on Si-doped Graphene: A Quantum Chemistry Study

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ABSTRACT

The functionalization of carbon based nanomaterials could have applications in atmospheric chemistry and contaminants removal. In this work, a quantum chemistry and computational kinetics study has been performed on the OH radical addition to ethylene previously adsorbed on a model surface of graphene. Rate constants are calculated and compared with the ethylene + OH gas phase reaction, for which experimental data are available. To the best of our knowledge, this is the first theoretical study of a reaction between a free radical and a molecule adsorbed on a graphene-type nanostructure.

Keywords: ethylene, graphene, coronene, reaction kinetics, Quantum Chemistry, Transition State Theory.

1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) occur in many natural environments where carbon is present. They are implicated in soot formation, in hydrocarbon combustion, and in the formation of dust grains in the interstellar medium. Coronene (C₂₄H₁₂) is the smallest PAH that presents the essential structural elements of graphite. Therefore, theoretical models of graphite, soot, or carbon nanotube walls often employ coronene as models representing a finite section of a carbon surface.

It is well-known that C and Si have completely different bonding characteristics, and that, instead of the characteristic carbon planar structures, silicon prefers 3-dimensional formations. Carbon atoms have been partially replaced by Si atoms in cage materials, and the synthesis of heterofullerenes containing up to 50% silicon atoms [1,2] and of silicon carbon nanotubes [3] has been reported. The presence of Si atoms in extended carbon compounds changes their electronic properties and chemical behavior. In particular, it is expected that extended polycyclic aromatic compounds with silicon defects may influence the atmospheric chemistry of unsaturated compounds.

In the troposphere, alkenes participate in a sequence of reactions which ultimately lead to their breakdown into highly toxic aldehydes, at the same time altering the equilibrium ratio of nitrogen oxides and indirectly producing ozone. [4]

In this work, quantum chemistry methods have been used to study the OH oxidation of ethene adsorbed on silicon doped graphene.

2 COMPUTATIONAL METHODOLOGY

Electronic structure calculations have been performed with the Gaussian03 program package [5]. Geometry optimizations of the stationary points along the coronene-ethylene + OH· reaction path have been performed using the hybrid density functional BHandHLYP [6,7], in conjunction with the 6-311G** basis set. Frequency calculations were carried out for all the studied systems at the same level of theory, and the character of the modeled structure was identified by the number of imaginary frequencies. Zero point energies (ZPE) and thermal corrections to Gibbs free energy at 298.15 K were included in the determination of the relative energies. Reaction Coordinate (IRC) [8] calculations were also performed to confirm that the transition states structures properly connect reactants and products. The rate constants were determined using Transition State Theory, [9,10] as implemented in the Rate 1.1 program.

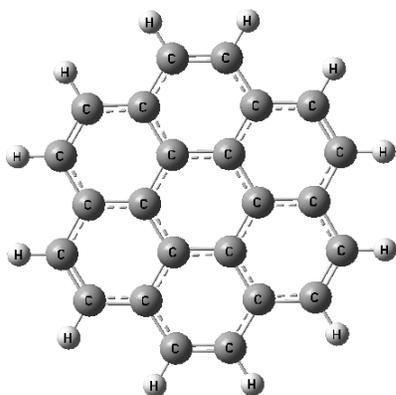
3 RESULTS AND DISCUSSION

3.1 Graphene Models

A coronene molecule and a Si doped coronene (2Si-coronene) have been used as models to represent graphene sheets. These systems have previously been used [11] to study the adsorption of thiophene on graphemes. These models are expected to retain the fundamental characteristics and chemistry of the systems of interest while, at the same time, rendering high-level calculations feasible. The graphene models are shown in Figure 1. While coronene is planar (a), 2Si-coronene is bent at the center (b).

3.2 Adsorption Complexes

Both adsorption complexes have been fully optimized at the hybrid functional BHandHLYP/6-311g(d,p) level (Figure 2). The ethylene molecule is allowed to move freely until it reaches the optimum adsorption site. In the complexes, the ethylene molecule is in a plane that is parallel and in the middle of the central ring.

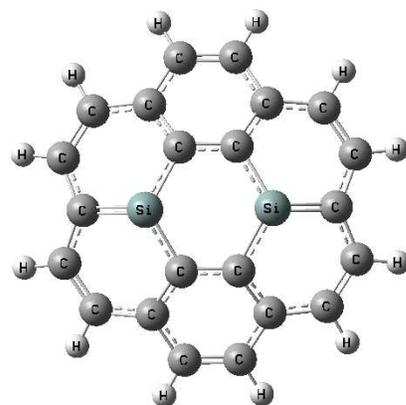


Top view

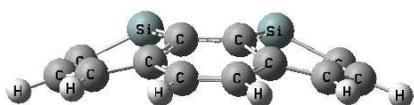


Side view

a) coronene



Top view



Side view

b) 2Si-coronene

Figure 1. Graphene surface models.

The adsorption energy is defined as the difference between the total electronic energy of the surface-adsorbate complex and the sum of those of the isolated molecule and the model surface, including ZPE corrections:

$$E_{\text{adsorption}} = E_{\text{adsorption complex}} - (E_{\text{molecule}} - E_{\text{surface}}) + \Delta(\text{ZPE}) \quad (1)$$

The ethylene molecule does not adsorb on coronene at all (a very shallow minimum, of less than 0.1 kcal/mol is obtained when ethene is more than 5 Å away from the surface), while the adsorption energy on 2Si-coronene is about -1.2 kcal/mol. The adsorption complex on 2Si-coronene is shown in Fig. 2, and relevant distances, in Å.

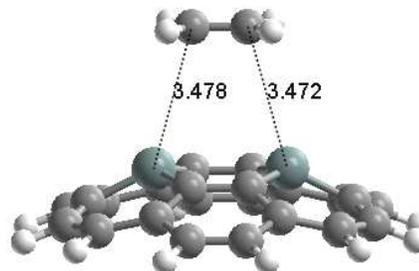
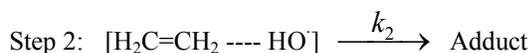
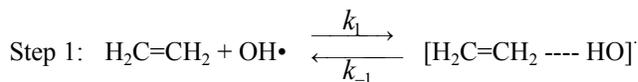


Figure 2. 2Si-coronene adsorption complex.

3.3 Reaction Mechanism

The OH reaction mechanism is assumed to be complex, and similar to the one observed in the gas phase. In the first step, the OH radical hydrogen atom interacts with the ethylene double bond and forms a pre-reactive Van der Waals intermediate, or reactants complex (RC), which is in equilibrium with the separated reactants. In the second step, the formation of a surface-ethylene-OH radical adduct is irreversible. All stationary structures are shown in Figure 3.



In general, the initial approach of the OH radical to the ethylene molecule is guided mainly by the Coulomb interaction between the positively charged hydrogen atom of the OH radical and the C=O double bond. For the adsorbed ethylene RC structure, shown in Figure 3, one can see that the Van der Waals distances between the surface and the ethylene molecule are slightly relaxed, while an H- π interaction takes place between the ethylene double bond and the radical hydrogen. In the case of the ethylene adsorbed on 2Si-coronene, the transition state is somewhat different to the one observed in the gas phase. It involves the breaking of the ethylene double bond and the simultaneous formation of *two* sigma bonds. One carbon atom attaches to the OH radical (as in the gas phase), while the other forms a covalent bond with coronene. Thus, a very stable radical product is obtained. In the radical adduct, the spin density is distributed over the coronene.

Energy values are calculated relative to the separated reactants, and are given in Table 1, including ZPE corrections. In order to take into account the entropy changes, Gibbs free energies are also included.

The energy profile obtained for the ethylene + OH reaction using the BHandHLYP/6-311G** energies is shown in Figure 3.

3.4 Reaction Kinetics

For the ethylene + OH· reaction, it has been shown that BHandHLYP/6-311G** quantum chemistry calculations

followed by conventional Transition State Theory rate constant calculations yield results that agree very well with experimental results in the gas phase. Therefore, one may assume that it is possible to use the same methodology to calculate reliable kinetic data for reactions on graphene surface models, for which experimental data are not available. The effective rate constant is obtained using the following equation:

$$k_{ef} = \sigma \kappa_2 \frac{Q^{TS}}{Q^R} \exp\left[-\frac{E_a^{eff}}{RT}\right] \quad (2)$$

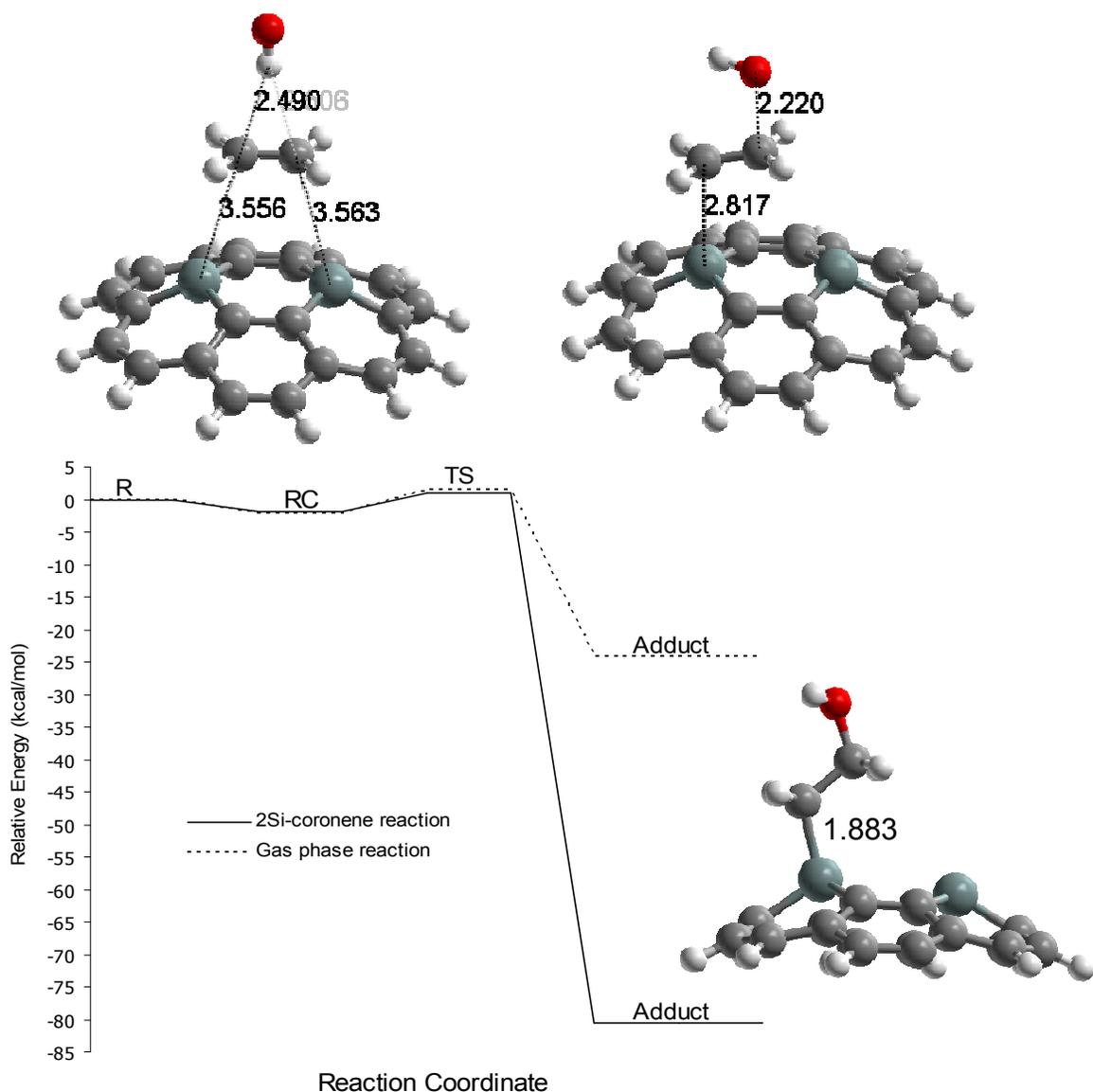


Figure 3. Energy profiles and optimized structures in the reaction ethylene + OH on 2Si-coronene.

Table 1. Relative energies including ZPE in kcal/mol and calculated rate constants (in cm³/molecule s) at 298 K. In this table, $E_{-1}=E_{RC}-E_R$; $E_2=E_{TS}-E_{RC}$; $E_a^{eff}=E_{TS}-E_R$; and $\Delta E=E_{products}-E_{reactants}$.

	E_{ads}	E_{-1}	E_2	E_a^{eff}	ΔE	ΔG	K_{eq}	k_2	k^{eff}
Gas phase	-	-2.12	3.64	1.52	-24.06	-16.64	1.81×10^{-22}	7.13×10^8	1.29×10^{-13}
2Si-Coronene	-1.19	-1.98	2.90	0.92	-80.58	-68.97	5.75×10^{-22}	4.76×10^7	2.73×10^{-14}

4 CONCLUSIONS

Physisorption processes of ethylene on coronene and 2Si-coronene have been studied using density functional theory methods. The calculated data show that the presence of silicon atoms favors the interaction of the surface model with ethylene and probably with other similar compounds. Small stabilization energies have been found. The ethylene physisorption on coronene is unlikely to occur, while that on 2Si-coronene leads to a stable addition product. In addition, the rate constant for the oxidation of ethene physisorbed on 2-Si-graphene is found to be an order of magnitude smaller than in the gas phase.

The results reported in this work suggest that silicon defects on extended polycyclic aromatic hydrocarbons, such as graphite, soot, and large-diameter carbon nanotubes, could make them useful in the removal processes of atmospheric pollutants.

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