Theoretical Studies on the Ozonization at the Capped-end of a Single-walled Carbon Nanotube: The Effect of the Finite Length

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ABSTRACT

The ozonization on the cap-ended site of the finite lengths (5,5) and (9,0) carbon nanotubes has been theoretically investigated by the density functional theory (PBE) with the basis set def-SV(P). The studies show that the 1,3 dipolar cycloaddition (1,3-DC) of ozone onto the end-capped site of carbon nanotubes is very facile, with a small activation energy of about 2 kcal/mol and a high exothermicity of 45 kcal/mol. It is interesting to note here that the reactivity of this reaction at the end-capped site of SWNTs is found to only weakly depend on the length of carbon nanotubes.

Keywords: ozonization, 1,3 dipolar cycloaddation, SWNTs, reaction mechanism, density functional theory (DFT)

1 INTRODUCTION

Single-walled carbon nanotubes (SWNTs) were discovered by S. Iijima in 1991 [1]. Since that time they have aroused considerable attention from researchers and have been the subject of numerous investigations for potential applications in nanotechnology. However, the purification and the potential applications of SWNTs have been impeded by their insolubility and high chemical stability. We believe that this impediment may be overcome by the chemical functionalization of SWNTs through the introduction of new physical and chemical properties and by increasing their solubility. Both experimental and theoretical reactions for the functionalization of carbon nanotubes have been the subjects of numerous reports [2]. These include several theoretical works which have focused on understanding the reaction of the 1,3-dipolar cycloaddition (1,3 DC) of ozone, considered to be one of the most facile reactions [3-8]. In a theoretical investigation of the ozonization on the SWNT using a 2-layered ONIOM (B3LYP/6-31G(d):AM1) scheme and a cluster model of C_{90}H_{30} as a model of the (5,5) tube, Lu et al. [3] have found that the activation energy for chemisorption of ozone on the sidewall of (5,5) SWNTS using periodic structure DFT calculations (PW91) with a plan-wave basis set and pseudopotentials for the atomic core region. They found that the activation and reaction energies of the ozonization reaction on a (5,5) SWNT is 5.9 and -11.7 kcal/mol, respectively. These latter results indicate that the exothermic energy obtained by the ONIOM method is substantially underestimated. In another study Yumura et al. [9-11] and Cioslowski et al. [12] revealed interesting results that the geometrical and electronic and thermo chemical properties of SWNTs depend strongly on the length of the tubes. It is, therefore, of interest to investigate the effect and reactivity of finite-length carbon nanotubes on the chemical reaction of ozone, which, to the best of our knowledge, have not been the subject of any reported theoretical study.

2 METHODOLOGY

The ozonization reaction on the finite-length SWNTs capped with fullerene hemispheres was investigated by cluster calculations performed with the TURBOMOLE code using the density functional method with the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE) and the def-SV(P) basis set which has a quality of about 6-j31G(d) basis set. For computational efficiency, all quantum calculations were performed using the resolution of identity density functional theory (RI-DFT). RI methods [13-14] are based on the approximate evaluation of the four-centered two-electron integrals. This approximation is calculated by using three-centered integrals, which are computationally less demanding and, therefore, considerably faster.

The finite-length nanotubes capped with fullerene hemispheres are considered in two series: (5,5) armchair nanotube series, C_{40+20n} \ (n=1-8), which belong to the D_{5d} symmetry point group, and (9,0) zigzag nanotube series, C_{60+18n} \ (n=1-8) which belong to the D_{3d} (D_{5d}) point group, even when \( n \) is odd. The armchair series (C_{40+20n}) and the zigzag series (C_{60+18n}). Geometrical structures of carbon nanotube complexes were fully optimized to determine the saddle point for the transition state structure (TS) and to find a local minimum for the 1,3 DC product. In addition, the frequencies were computed to verify that the optimized
transition state connects the intended reactant and product. Previous studies [15-17] regarding chemical reaction on C$_{60}$ showed that the C1-C2 site is more dipolarophilic than other sites in C$_{60}$. Therefore, in this study, in the end-capped site, which has a structure like a hemisphere of C$_{60}$ material, we considered only the C1-C2 pair site as an active site.

Figure 1: (a) Top view of carbon nanotubes with labeled carbon atoms; (b) Presentation of the (5,5) armchair nanotube series, C$_{40+20n}$ (n=1-8) and (9,0) zigzag nanotube series, C$_{60+18n}$ (n=1-8).

3 RESULTS AND DISCUSSION

Geometry-optimized structures of the armchair and zigzag series were carried out by using the PBE/def-SV(P) level of theory. For the armchair series, it was found that, at the hemisphere-capped site, the C1-C2 bond distance was slightly lengthened from 1.398 Å to about 1.411 Å when the tube length was increased, while the bond lengths of C-C bonds neighboring the C1-C2 bond did not change much from 1.45 Å when increasing the length of the tube. In the case of the zigzag series, a similar observation was noted where there was also a slight increase of the C1-C2 bond when the length of the tube was increased.

Figure 2, shows that the HOMO-LUMO gaps of the armchair series oscillate with the increase of the tube length, while in the zigzag series, the gaps decrease with the lengthening of the tubes. These results are similar to those of previous studies [10, 12], using the B3LYP level of theory. The oscillating behavior in the gaps of the armchair series is due mainly to the interchain interactions in the armchair series [10]. The gaps of the zigzag series do not oscillate with the tube lengths, due to the nodal properties of the trans-polyene chains [10].

The changes of the C1-C2 bond distances of the initial nanotubes, the transition states and the products as a function of the tube length are shown in Figure 3. In the transition state structure (TS), the C1-C2 bond is slightly elongated by about 0.02 Å to a value of ~1.43 Å both in the armchair and in the zigzag series. While, the C1-C2 bond length in the product is about 1.60 Å, which is longer than the typical C-C single bond (~1.54 Å). The small elongation of the C1-C2 bond distance at the TS suggests that this reaction has an “early” transition state which requires a little activation energy. The increase in the tube length does not have any significant effect on the TS structures.

The computed activation energy for the cycloaddition of ozone is about 2 kcal/mol, both on the armchair and zigzag series and is independent of the tube length (see Fig. 4). These barriers are comparable to the value which has been reported in literature for the investigation of ozonization at the sidewall of (5,5) single-walled carbon nanotubes [5]. The 1,3-DC product on the end-capped site is exothermically predicted to be ~45 kcal/mol, which is more exothermic than that of the reaction at the sidewall ozonide [5] by about 35 kcal/mol. This means that ozone would thermodynamically be more favorable to react at the end-capped site than at the sidewall of carbon nanotubes. Furthermore, it was found that the length of carbon nanotubes has an insignificant impact on the reactivity at the end-capped site of SWNTs.

Figure 2: HOMO-LUMO gaps as a function of the number of cyclic polyene chains in the finite length at the PBE/def-SV(P) level of theory.
Figure 3: C1-C2 bond distance in complexes; isolated Carbon nanotubes, TS and product, respectively.

Figure 4: (a) Reaction mechanism of ozonization at the end-capped site of carbon nanotubes; (b) Energetic profiles of the ozonization of the finite-length nanotubes capped with the fullerene hemispheres: (5,5) armchair nanotube series, \( C_{40+20n} \) and (9,0) zigzag nanotube series, \( C_{60+18n} \), respectively.
4 CONCLUSION

The 1,3-DC of ozone onto the end-capped site of fullerene hemisphere-capped carbon nanotubes has been investigated by means of the PBE/def-SV(P). In the finite length armchair, C_{40+20n} and zigzag, C_{60+18n} nanotubes, the calculation revealed that the reactivity of 1,3-DC of ozone at the end-capped site of SWNTs is a very facile reaction and is independent of the tube length and the type of nanotubes, despite the fact that the electronic properties are strongly dependent on the type and the length of the SWNTs. The activation energy for ozonization onto the end-capped site is ~2 kcal/mol and the reaction energy is highly exothermic, -45 kcal/mol.

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REFERENCES