

# Can the Sidewalls of Single-Wall Carbon Nanotubes Be Ozonized?

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Received: September 11, 2001; In Final Form: November 29, 2001

Ozonization of the sidewalls of single-wall carbon nanotubes (SWNT) has been investigated by means of 2-layered ONIOM(B3LYP/6-31G\*:AM1) calculations. The theoretical calculations reveal that the 1,3-dipolar cycloaddition (1,3-DC) of ozone ( $O_3$ ) onto the sidewalls of a (5,5) carbon nanotube is site-selective and facile with a small activation barrier of 1.4 kcal/mol. The desorption of ozone from the thus-formed ozonide was found to be favorable over the decomposition process that gives rise to epoxy adduct and  $O_2$  upon thermal activation. This work implies the possibility of functionalizing the sidewalls of SWNTs by means of 1,3-dipolar cycloadditions of 1,3-dipolar molecules.

## I. Introduction

Since their discovery in 1991,<sup>1</sup> single-wall carbon nanotubes (SWNTs) have attracted much attention owing to their unique structural, mechanical, electrical, and electromechanical properties.<sup>2–4</sup> Chemical modification of SWNTs, especially the sidewall functionalization, is of particular interest that may introduce new physical and chemical properties for specific applications, such as soluble nanotubes,<sup>5–8</sup> self-assembly on surfaces, chemical sensors,<sup>9–11</sup> protein immobilization,<sup>12</sup> and so forth. However, there have been limited ways so far reported for the sidewall functionalization of SWNTs, e.g., fluorination at elevated temperature,<sup>13</sup> noncovalent attachment of a bifunctional molecule (1-pyrenebutanoic acid, succinimidyl ester),<sup>12</sup> and electrochemical reduction of aryl diazonium salts.<sup>14</sup> We have recently performed a theoretical investigation concerning the ozonization of the sidewall of single-wall carbon nanotubes and present the results herein.

Ozone is an 18-valence-electron 1,3-dipolar molecule that undergoes 1,3-dipolar cycloaddition (1,3-DC) reaction with olefins followed by complicated decomposition/isomerization of the thus-formed primary ozonide (POZ).<sup>15–18</sup> Such an ozonolysis process of olefins follows the Criegee's mechanism,<sup>17</sup> as demonstrated in Figure 1. The first step, i.e., the 1,3-DC reaction, is quite facile with a small activation energy (e.g., around 5 kcal/mol for the gas-phase reaction of ozone with ethylene).<sup>18</sup> Similar ozonization process has been found to occur on the highly  $\pi$ -conjugated  $C_{60}$ , producing the intermediate-like fullerene ozonide ( $C_{60}O_3$ ) followed by the formation of  $C_{60}O$  which reacts further to produce  $C_{60}O_2$  (see for example refs 19–23). These chemical precedents imply that analogous reaction might take place on the sidewall of SWNT.

The first experimental study of ozone reaction with carbon nanotubes was reported briefly by Deng et al. in 1997.<sup>22,23</sup> Very recently, Mawhinney et al. reported FTIR spectroscopic studies of the oxidation and etching of SWNTs using ozone at 298 K, and the subsequent thermal stability of the oxygenated groups.<sup>24</sup> The ozonolysis reaction was found to occur at the end caps of the SWNTs, producing two distinct surface bound functional

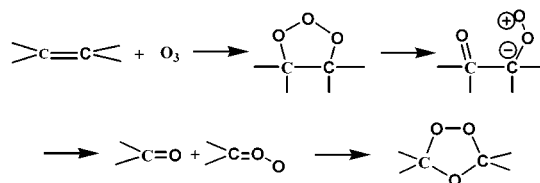


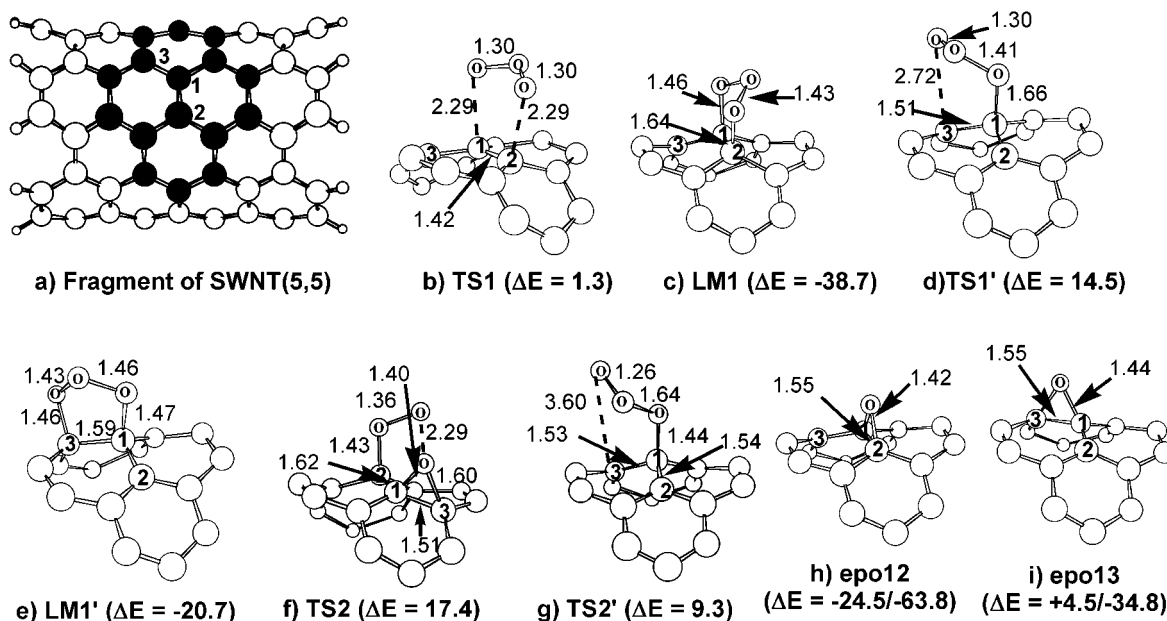
Figure 1. Criegee's mechanism of ozone with olefin.

groups, esters and quinones, as well as  $CO_2$  and  $CO$ . The structural integrity of the nanotube walls was maintained during the oxidation reaction.<sup>24</sup> The enhanced reactivity of the end caps and kink sites, compared to the reactivity of the walls, can be understood by the increased strain at these sites causing a partial loss of conjugation.<sup>25</sup> However, the curvature of the SWNT sidewall and the high reactivity of ozone toward  $C=C$  double bonds implies that one could not exclude the possibility of 1,3-DC of ozone onto the sidewalls of SWNTs, especially for those with small diameters. To confirm the inference, we performed quantum chemical cluster model calculations concerning the 1,3-DC reaction of ozone onto the sidewalls of a (5,5) carbon nanotube. The results showed that the ozonization is facile with only a small activation barrier.

## II. Computational Details

A 2-layered ONIOM approach is used.<sup>26</sup> The semiempirical AM1 method<sup>27</sup> and the hybrid density functional B3LYP method<sup>28,29</sup> are employed for the low-level and high-level treatments, respectively. The standard 6-31G\* basis set is used in conjunction with the B3LYP calculations. The ONIOM calculations were performed using the Gaussian98 program.<sup>30</sup> As shown in Figure 2(a), a fragment of SWNT(5,5) that consists of totally 90 carbon atoms is used. The dangling bonds at the ends are saturated with hydrogen atoms. This gives a  $C_{90}H_{20}$  tube. Sixteen carbon atoms, at the center of the  $C_{90}H_{20}$  tube (see the shaded atoms in Figure 1(a)), in together with ten H atoms as boundary atoms are used for the high-level treatment. Ozone is then bonded to the high-level part of the cluster. It should be pointed out that at the sidewalls of a (5,5) carbon nanotube, there are two types of inequivalent C–C pair sites, i.e., the 1,2 pair site and the 1,3 pair site, available for the 1,3-DC of ozone, as shown in Figure 1(a).

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**Figure 2.** Reactants, transition states, and products for the ozonization of a (5,5) carbon nanotube. (a) a fragment of SWNT(5,5), in which the 24 shaded carbon atoms comprising of the high-level part in the 2-layered ONIOM(B3LYP:AM1) calculations; (b) TS1; (c) LM1; (d) TS2; (e) LM2; (f) TS3; (g) TS4; (h) ep1 and (i) ep2. Energies ( $\Delta E$ , in kcal/mol) relative to the initial reactants are given in parentheses.

Geometry optimizations are performed within the ONIOM approach. For the  $C_{90}H_{20}$  model tube, the optimized C–C bond lengths range within 1.38 Å to 1.46 Å, deviated by no more than 0.04 Å from the bulk value (1.42 Å) of graphite. It is worth mentioning that the ONIOM approach has recently been employed in the theoretical investigation of hydrogen and fluorine binding to the sidewalls of a (10,0) carbon nanotube.<sup>31</sup> Furthermore, a longer model tube,  $C_{130}H_{20}$ , along with the same high-level inner cluster was examined to check convergence of model tube length. No significant differences were found in the calculated energies and the geometries for ozonide adduct on the 1,2 pair site. The reported computed data below were obtained with the  $C_{90}H_{20}$  model tube.

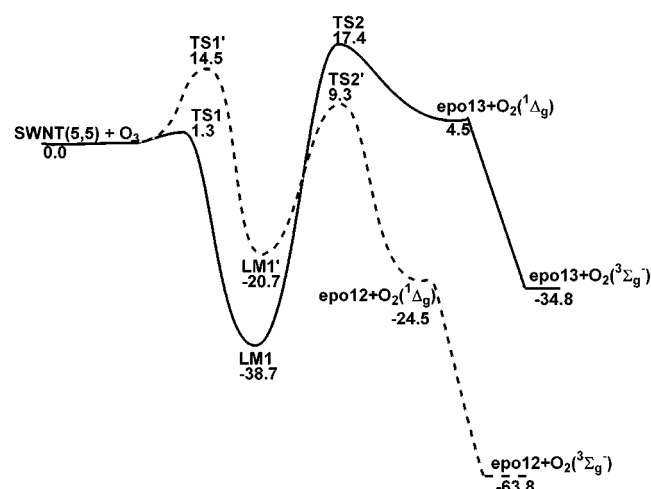
### III. Results and Discussion

We first considered the 1,3-DC of ozone onto the 1,2 pair site. The optimized geometries of the transition state (TS1) and 1,3-DC product (LM1) are given in Figure 1(b) and (c), respectively. In TS1 (Figure 1(b)), the C1–C2 bond is elongated by 0.04 Å from the original bond length of 1.38 Å; the lengths of the two forming O–C bonds are equivalently in a value of 2.29 Å. It is thus clear that the 1,3-DC of ozone onto the 1,2-pair site follows a concerted pathway. The predicted barrier height at TS1 is only 1.4 kcal/mol, showing the 1,3-DC on C1–C2 is quite facile. In the 1,3-DC product (LM1), the C1–C2 bond length is 1.64 Å, which is typical of the C–C single bond; the C–O bond lengths and the O–O bond lengths are 1.46 and 1.43 Å, respectively. The binding energy of the ozonide species formed by 1,3-DC is predicted to be 38.7 kcal/mol, i.e., the 1,3-DC of ozone onto the C1–C2 site is exothermic.

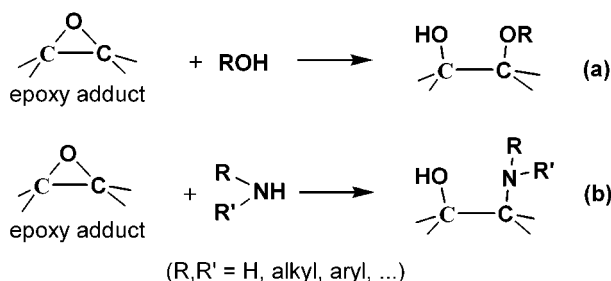
We then consider the 1,3-DC of ozone onto the 1,3 pair site. For this process, a transition state (TS1') was located, which is depicted in Figure 2(d). In TS1', the lengths of the two forming C–O bonds are 1.66 Å (C1–O) and 2.72 Å (C3–O), respectively. The structural feature indicates that in contrast to the concerted 1,3-DC of ozone onto the 1,2 pair site, the 1,3-DC of ozone onto the C1–C3 pair site follows an asynchronous pathway. The barrier height of this asynchronous 1,3-DC process on the C1–C3 pair site is predicted to be 14.5 kcal/mol, by

13.1 kcal/mol higher than that of the concerted 1,3-DC on the C1–C2 pair site. Meanwhile, the 1,3-DC product (LM1') on the C1–C3 pair site is predicted to have a smaller binding energy (20.7 kcal/mol) than that on the C1–C2 pair site. Hence, the 1,3-DC of ozone onto the C1–C2 pair site is both kinetically and thermodynamically favorable over the 1,3-DC on the C1–C3 pair site. It means that ozone would selectively adsorb onto the C1–C2 pair site when ozonizing the sidewalls of a (5,5) nanotube.

Further decomposition/isomerization of the thus formed ozonide adducts (LM1 and LM1') have been also considered. It is expected that similar to the decomposition/isomerization of ozonide species on  $C_{60}$ , the decomposition of ozonide on the sidewalls of a (5,5) nanotube would produce epoxy adduct and singlet  $O_2$  ( $^1\Delta_g$ ) which can be immediately quenched into triplet  $O_2$  ( $^3\Sigma_g^-$ ). Starting from LM1, the ozonide adduct was found to decompose through a transition state (TS2 in Figure 1(f)), producing an epoxy adduct (epo13 in Figure 1(i)) onto the 1,3 pair site along with the elimination of singlet  $O_2$ . Such a decomposition process requires a quite large activation energy of 56.1 kcal/mol and is endothermic of 43.2 kcal/mol with respect to LM1. The result that TS2 is by 17.4 kcal/mol higher in energy than the initial reactants suggests that upon thermal activation, the ozonide species would preferentially desorb than decompose into epoxy adduct and  $O_2$ . Such an argument is also supported by the finding that the decomposition product, epo13 plus singlet  $O_2$ , is by 4.5 kcal/mol higher in energy than the initial reactants. Furthermore, the decomposition of ozonide in LM1' is found to be much easier than that in LM1. This process has to overcome a barrier height of 30 kcal/mol at the transition state TS2' (see Figure 1(g)) and produces an epoxy adduct (epo12 in Figure 1(h)) at the C1–C2 pair and singlet  $O_2$ . This process is found to be exothermic by –3.8 kcal/mol with respect to LM1'. This means that with respect to the initial reactants (unreacted (5,5) tube plus ozone), the formation of epoxy adduct (epo12) at the C1–C2 pair site and singlet  $O_2$  is thermodynamically favorable with a predicted exothermicity of –24.5 kcal/mol, but kinetically unfavorable given the large activation energy



**Figure 3.** Profile of energy surface for ozone with a (5,5) nanotube. (Solid line for the reaction over the 1,2 pair site and dashed line for the reaction on the 1,3 pair site.



**Figure 4.** Proposed mechanisms for anchoring other organic groups by epoxy adducts on the sidewall of the SWNT with alcohols and amines.

(14.5 kcal/mol) required for the formation of the precursor ozonide on the 1,3 pair site.

The profile of energy surface for the processes concerned above is depicted in Figure 3, which clearly shows that the 1,3-DC of ozone onto the 1,2 pair site is facile and the thus-formed ozonide prefers to desorb as  $O_3$  than to decompose into epoxy adduct and  $O_2$  upon thermal activation.

#### IV. Concluding Remarks

In summary, our 2-layered ONIOM(B3LYP/6-31G\*:AM1) calculations reveal that the 1,3-dipolar cycloaddition of ozone onto the sidewalls of a (5,5) carbon nanotube is site-selective and facile on the 1,2-pair site. The desorption of ozone from the thus-formed ozonide was found to be favorable over the decomposition process that gives rise to epoxy adduct and  $O_2$  upon thermal activation. The theoretical finding suggests a plausible way to chemically modify carbon nanotube by ozone and implies the possibility of functionalizing the sidewalls of SWNTs by means of 1,3-dipolar cycloadditions of 1,3-dipolar molecules, which also deserves further theoretical and experimental investigations. On the other hand, though the thermolysis of ozonide adduct into epoxy adduct seems less advantageous, the photolysis of ozonide<sup>20,21</sup> could be plausible to give rise to epoxy adduct on the sidewall of the SWNT. It is well-known that epoxides are very reactive to nucleophilic agents such as water ( $H_2O$ ), alcohol ( $ROH$ ), ammonia ( $NH_3$ ) and primary and secondary amines.<sup>32</sup> Hence, the epoxy adducts on the sidewalls of a SWNT, if subject to similar reactions, can be used to anchor a wide variety of functional groups along with hydroxyl (OH) adduct onto the sidewall of a SWNT, as schematically shown

in Figure 4. This opens up ways to functionalize SWNTs with desired functional groups for specific use.

Finally, it should be mentioned that the reactivity of the sidewalls of carbon nanotubes depends largely on the tube wall curvature.<sup>33,34</sup> The (5,5) nanotube investigated in the present work is among those of the smallest SWNTs that can be experimentally synthesized<sup>35</sup> and, meanwhile, offer high feasibility for theoretical study.<sup>11,33,34,36,37</sup> This means that the results presented here should be considered to be only an upper bound of the reactivity of realistic samples. Further theoretical work is on the way to investigate to what extent the curvature of the sidewalls of SWNTs affects the reactivity of its C–C pair site to the in-coming ozone.

**Acknowledgment.** This work is supported by the Natural Science Foundation of China, the Ministry of Education of China, Fok Ying-Dung Educational Foundation and Xiamen University.

**Note Added in Proof.** The 1,3-dipolar cycloaddition of azomethine ylides onto carbon nanotube was realized very recently by Prato et al. (Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760).

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