ONIOM Studies of Esterification at Oxidized Carbon Nanotube Tips

F F Contreras-Torres and V A Basiuk
Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior C.U., A. Postal 70-543, 04510 México D. F., Mexico
E-mail: flavioc@nucleares.unam.mx

Abstract. Esterification of oxidized carbon nanotubes (CNTs) can open a new route for the separation of zigzag and armchair nanotubes. We studied theoretically (by using hybrid DFT within the ONIOM embedding protocol) the reactions of monocarboxy-substituted oxidized tips of zigzag and armchair single-walled CNTs (SWCNTs) with methanol. According to the calculated values of activation energy, Gibbs free-activation barriers, and enthalpies of formation for the SWCNT−(COOH)H5 models, the zigzag nanotube isomer is more reactive as compared to its armchair counterpart. For other models we obtained variable results.

1. Introduction
The unique chemical, physical, structural, electronic and mechanical properties typical for carbon nanotubes (CNTs) can hardly be found simultaneously in any other chemical compound or material. CNTs can exhibit either metallic or semiconductor conductivity. Unfortunately, these electronic properties cannot be efficiently employed in nanotechnology on a large scale, because of the difficulty to separate different forms of CNTs. Modern computational methods can help to study physical and chemical properties of CNTs and to predict efficient ways of separating their different chiral forms. Nevertheless, related calculations of thermodynamics and mechanisms of chemical reactions are extremely computationally demanding due to a large size of these carbon clusters, and therefore remain to be a challenging task. One of the most promising theoretical approaches capable of treating large molecular systems is based on the combined Quantum Mechanical/Molecular Mechanical (QM/MM) models, in particular the two or three-level ONIOM method [1]. It implies dividing a large molecular system into two or three theoretical levels. A relatively small section, crucial for studying the property of interest, is treated at a higher theoretical level (usually ab initio or DFT). The remaining one or two layers, serving mostly to constrain the general geometry, are described by a computationally less demanding method (force field or semi-empirical methods). Due to the above advantage, the ONIOM approach became an indispensable tool to study chemical structure, reactivity, and spectral properties of single-walled carbon nanotubes (SWCNTs) [2].

Recently we studied theoretically (with the ONIOM B3LYP/6-31G(d):UFF computation scheme) the direct esterification of monocarboxy-substituted tips of zigzag and armchair SWCNTs with methanol [3]. Along with the direct (thermally activated) amidation [4-7], this reaction is considered especially important for SWCNT chemistry. One of the reason is that revealing the energetic preference in the direct formation of amides and esters on armchair SWCNT tips versus zigzag nanotube tips might open a new route to selective derivatization of different forms of SWCNTs, and
thus helping their separation and purification due to differences in solubility. In the previous ONIOM study [2], the formation of ester derivatives on carboxylated armchair SWCNT tips was found to be more energetically preferable as compared to that on the zigzag nanotube ones. Nevertheless, the possibility of purely mathematical artifacts still cannot be excluded, since in those SWCNT models, the higher level was limited to one aromatic ring with COOH group and a few neighboring atoms.

In the present work, to further study the esterification reaction at oxidized SWCNT tips we attempted expanding the higher ONIOM level to six fused aromatic rings. In addition to that, we varied the structure of terminal functional groups (different combinations of carboxylic, hydroxylic and quinone groups) to better match the real chemical nature of oxidized SWCNT defects.

2. Computational Details
The Gaussian 03W suite of program [8] was used to carry on all calculations. As was implemented in Gaussian, we used a QM/MM hybrid technique to take advantage of cutting the whole system in two parts, by employing the ONIOM embedding protocol [1]. A small but critical part, which determines the entire process of esterification reaction, was studied with the hybrid B3LYP density functional. Due to a large size of the resulting higher-level cluster, we had to reduce the basis set to STO-3G. The remaining large segment, which served to simply keep the tubular geometry, was treated with Universal Force Field (UFF). The stationary point geometry’s were fully optimized and characterized as either minima (no imaginary frequency) or first-order saddle points (one imaginary frequency) by performing force constants calculations at every SCF step.

3. Results and Discussion
All nanotube structures studied are specified in the Fig. 1 (A = armchair and Z = zigzag forms).

The chemical reaction under the study can be described as follows:

\[
\text{SWCNT-COOH} + \text{HOCH}_3 \rightarrow \text{SWCNT-} \overset{\text{C(=O)-OCH}_3 + \text{H}_2\text{O}}{\text{C}}
\]  

(1)

To study this reaction, we selected three models of oxidized SWCNTs tips, using different possible combinations of oxygenated functionalities. These models, shown in Fig. 1, are (COOH)H\text{5}, (COOH)OH(=O)\text{4} and (COOH)\text{3}(OH)\text{3}, for both armchair A(9,9) and zigzag Z(16,0) nanotubes. Tables 1-3 summarize the energies (in kcal mol\textsuperscript{-1}) of reaction complexes (RCs), transition states (TSs) and products (Ps). In all cases, these energies are relative values attributed to the total energies of separated reactants, that is oxidized SWCNT and MeOH, according to the Hess’s Law. The SCF B3LYP,
ONIOM extrapolated and ZPE-ONIOM correction energies are reported for comparison. Finally, Table 4 shows thermodynamic values and kinetic constants (calculated for 298 and 498 K) by taking the reactants as the reference state by using $c^0 = 1$ as initial concentration.

### 3.1. (COOH)$_5$ Model

As a whole, the geometries of RCs, TSs and Ps keep the most important features observed in the previous calculations at the HF/STO-3G:UFF theoretical level [2]. However, contrary to our expectations, energetic values and general trends are not the same. From the values in Table 1, differences between SCF B3LYP and ONIOM extrapolated energies are 7-kcal mol$^{-1}$ for armchair and just only 2-kcal mol$^{-1}$ for zigzag; that is, the last strongly depend on the nanotube chirality. Only the SCF B3LYP energies will be discussed in detail. According to the positive relative energies of Ps, the esterification is endothermic for both armchair and zigzag nanotubes. However, the TS energies are higher for the armchair nanotube as compared to its zigzag counterpart; in other words, the reaction (1) is more favorable thermodynamically for the zigzag nanotube for this particular model. The same conclusion can be made from the values in Table 4, where Gibbs free-activation barriers $\Delta G^\ddagger$ are 38 and 32 kcal mol$^{-1}$ for armchair and zigzag, respectively. Also, the kinetic constants calculated for 298 and 498 K show that the zigzag reaction is more favorable than the armchair one, for example by $10^{10}$ at 498 K.

#### Table 1. Energies (in kcal mol$^{-1}$)$^a$ relative to the level of SWCNT and methanol reactants for reaction complexes (RCs), transitions states (TSs) and hydrogen-bonded products (Ps) in the gas-phase esterification reaction of SWCNT-$(COOH)H_5$ nanotubes with MeOH, calculated at the B3LYP/STO-3G:UFF level of theory.

| Stationary point | B3LYP  | ONIOM | ZPE-ONIOM |
|------------------|--------|-------|-----------|
| A-RC             | -35.5  | -28.4 | -24.2     |
| A-TS             | 22.9   | 30.3  | 32.9      |
| A-P              | 3.4    | 10.7  | 12.6      |
| Z-RC             | -4.8   | -3.2  | -1.9      |
| Z-TS             | 16.9   | 18.7  | 20.0      |
| Z-P              | 3.4    | 5.3   | 5.5       |

$^a$ The relative energies were calculated according to the following formula: $\Delta E_x = E_x - (E_{SWCNT} + E_{MeOH})$ where $E$ is absolute energy; $x$ is RC, TS or P; SWCNT is carboxy-substituted nanotube (Fig. 1).

The (COOH)$_5$ model is the least realistic one, since the oxidative purification of SWCNTs cannot produce C-H groups at the nanotube edges; the reported values serve just as a benchmark reference.

### 3.2. (COOH)OH(=O)$_4$ Model

The thermodynamic results for this model were as follows (Table 2). The reaction was endothermic by 0.8-kcal mol$^{-1}$ for the armchair SWCNT, whereas for the zigzag nanotube it was -11.3 kcal mol$^{-1}$ exothermic. The TS energy was 72.6 kcal mol$^{-1}$ for the zigzag SWCNT. Surprisingly, a value of -16.1 kcal mol$^{-1}$ was calculated for its armchair counterpart. A closer consideration showed that the first-order saddle point found is irrelevant to the esterification reaction; however, several attempt to find the correct Transition State failed. This failure might be particularly associated with the use of minimal basis set STO-3G. The kinetic constant $K_{498} = 2.1 \times 10^{25}$ for the zigzag nanotube is so small that this reaction can hardly proceed even at higher temperatures.
Table 2. Energies (in kcal mol\(^{-1}\)) relative to the level of SWCNT and methanol reactants for reaction complexes (RCs), transitions states (TSs) and hydrogen-bonded products (Ps) in the gas-phase esterification reaction of SWCNT-(COOH)OH(=O)\(_4\) nanotubes with MeOH, calculated at the B3LYP/STO-3G:UFF level of theory.

| Model   | B3LYP  | ONIOM  | ZPE-ONIOM |
|---------|--------|--------|-----------|
| A-RC    | -20.2  | -13.7  | -9.1      |
| A-TS    | -16.1  | -9.7   | -5.8      |
| A-P     | 0.8    | 7.5    | 9.9       |
| Z-RC    | 27.7   | 24.8   | 24.1      |
| Z-TS    | 72.6   | 69.2   | 67.1      |
| Z-P     | -11.3  | -11.6  | -9.8      |

3.3. \((\text{COOH})_3(\text{OH})_3\) Model

This reaction is endothermic by 43-kcal mol\(^{-1}\) for the armchair nanotube, and exothermic by 9-kcal mol\(^{-1}\) for the zigzag SWCNT; the corresponding B3LYP transition state energies were 29 and 2 kcal mol\(^{-1}\). Again, the latter value seemed too low, and a closer analysis of Z-TS geometry showed that the first-order saddle point found is irrelevant to the esterification reaction. A few attempts to calculate the correct Transition State failed, leaving the available set of energy values incomplete. The calculated kinetic constant for A (9,9)-(COOH)_3(OH)_3 at 498 K is \(K_{498} = 2.1 \times 10^{07}\).

Table 3. Energies (in kcal mol\(^{-1}\)) relative to the level of SWCNT and methanol reactants for reaction complexes (RCs), transitions states (TSs) and hydrogen-bonded products (Ps) in the gas-phase esterification reaction of SWCNT-(COOH)_3(OH)_3 nanotubes with MeOH, calculated at the B3LYP/STO-3G:UFF level of theory.

| Model   | B3LYP  | ONIOM  | ZPE-ONIOM |
|---------|--------|--------|-----------|
| A-RC    | -25.8  | -20.5  | -15.2     |
| A-TS    | 29.3   | 36.1   | 39.0      |
| A-P     | -42.7  | -35.3  | -29.4     |
| Z-RC    | -47.5  | -63.3  | -62.9     |
| Z-TS    | 2.4    | -15.2  | -17.3     |
| Z-P     | 8.7    | -8.7   | -11.2     |

4. Conclusions

The thermodynamic results obtained are poorly concordant both between them and with the previously reported values [2] calculated at the HF/STO-3G:UFF level, thus rising a question of what set of the values is most credible at the B3LYP/STO-3G:UFF level of theory. The \((\text{COOH})_3(\text{OH})_3\) models can match the contribution of carboxylic and hydroxyl groups into the chemistry of oxidized SWCNTs; however, they do not include quinone functionality. In addition to that, so high density of COOH groups is hardly possible for steric reasons. The latter factor must have an especially strong effect on the calculated energies. Apparently, the (COOH)OH(=O)\(_4\) models and the corresponding results can be considered as the most realistic ones. However, the thermodynamic data presented here are merely insufficient to make a conclusion. The main reason is that the ONIOM B3LYP/STO-3G:UFF technique employed sometimes fails to find relevant Transition States.
Table 4. Values (in kcal mol\(^{-1}\)) of electronic energies \(\Delta E_a\), Gibbs free-activation barriers \(\Delta G^f\) (relatives to the level of reactant nanotubes and MeOH) and enthalpies of formation \(\Delta H_f\) calculated at the B3LYP/STO-3G:UFF level of theory, for transitions states (TSs) and hydrogen-bonded products (Ps) in (1). Constants kinetics (in s\(^{-1}\) L mol\(^{-1}\)) \(^a\) at 298 and 498 K.

| Reactions | \(\Delta E_a\) | \(\Delta H_f\) | \(\Delta G^f\) | \(K_{reaction}\) |
|-----------|----------------|---------------|---------------|------------------|
| (COOH)H\(_5\) |               |               |               |                  |
| A-TS      | 22.9           | 38.2          | 6.2\times10^{-16} | 1.8\times10^{11} |
| A-P       | 3.4            | 39.0          |               |                  |
| Z-TS      | 16.9           | 32.1          | 1.8\times10^{-11} | 0.9\times10^{1}  |
| Z-P       | 3.4            | 8.2           |               |                  |
| (COOH)OH(=O)\(_4\) |           |               |               |                  |
| A-TS      | -16.1          | 0.1           | (5.2\times10^{12})\(^b\) | (9.4\times10^{12})\(^b\) |
| A-P       | 0.8            | 21.2          |               |                  |
| Z-TS      | 72.6           | 85.9          | 6.6\times10^{-51} | 2.1\times10^{25} |
| Z-P       | -11.3          | 39.0          |               |                  |
| (COOH)\(_3\)(OH)\(_3\) |           |               |               |                  |
| A-TS      | 29.3           | 44.9          | 7.6\times10^{-21} | 2.1\times10^{7}  |
| A-P       | -42.7          | -16.8         |               |                  |
| Z-TS      | 2.4            | 14.0          | (3.4\times10^{5})\(^b\) | (7.5\times10^{6})\(^b\) |
| Z-P       | 8.7            | 56.2          |               |                  |

\(^a\) These values were calculated according to the general Theory of Transition State. All energies specified were calculated by using only SCF B3LYP energies. \(^b\) These transition states turned to be irrelevant to the esterification reaction (1).

Although ONIOM method was capable of providing important thermodynamic values for minima, it is highly desirable to explore all the models by using a larger basis set (i.e. 3-21G\(^*\)) especially for TS structures.

Acknowledgements The authors appreciate financial support from the National Autonomous University of Mexico (grant DGAPA-IN100303). F.F.C.-T. thanks DGEP UNAM.

References
[1] Dapprich S, Komáromi I, Byun K S, Morokuma K and Frisch M J 1999 J. Mol. Struct. (Theochem) 461 1
[2] Basiuk V A and Contreras-Torres F F 2006 Encyclopedia of Nanoscience and Nanotechnology, ed H S Nalwa (American Scientific Publishers: Stevenson Ranch CA) in press
[3] Basiuk V A 2002 Nano Lett. 2 835
[4] Basiuk V A, Basiuk E V and Saniger-Blesa J M 2001 Nano Lett. 1 657
[5] Basiuk V A 2003 J. Phys. Chem. B 107 8890
[6] Basiuk V A 2004 J. Nanosci. Nanotechnol. 4 1095
[7] Basiuk V A 2004 J. Comput. Theor. Nanosci. 1 378
[8] Frisch M J et al. 2003 Gaussian 03W Revision B.04 (Gaussian Inc.: Pittsburg PA)