Sidewall Oxidation and Complexation of Carbon Nanotubes by Base-Catalyzed Cycloaddition of Transition Metal Oxide: A Theoretical Prediction

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ABSTRACT

By means of a two-layered ONIOM (B3LYP/LANL2DZ:UFF) approach, we predicted the viable oxidation of the sidewalls of single-wall carbon nanotubes by transition metal oxide (OsO_4), which gives rise to osmate ester adducts on the nanotube sidewall. We believe that the as-formed osmate ester adducts can be a good starting point for further functionalization, hence, introducing high flexibility to carbon nanotubes for further manipulations for various potential applications.

Single-wall carbon nanotubes (SWNTs) have very recently invoked intensive interest owing to their fascinating structural, mechanical, electrical, and electromechanical properties.[1−4] With graphene-like structures, they display, however, quite high chemical stability and notorious insolubility and, as a consequence, low flexibility to be modified chemically for various applications. Accordingly, it is highly desirable to obtain better understanding of the chemistry of SWNTs for rational manipulation of their properties. Much effort has been made recently focusing on the chemical modification of SWNTs,[5−19] especially the sidewall functionalization by, for example, fluorination at elevated temperature,[12] non-covalent attachment of a bifunctional molecule (1-pyrenebutaboic acid, succinimidyl ester),[13] electrochemical reduction of aryl diazonium salts,[14] covalent attachment of nitrenes,[15] and 1,3-dipolar cycloadditions of azomethine ylides and ozone.[16,17] The latter findings are rather stimulating, as they demonstrated the curvature-induced chemical reactivity of the nanotube sidewalls and, more significantly, the plausibility of functionalizing the sidewalls of SWNTs by means of synthetic organic chemistry. On the other hand, attempts to employ carbon nanotubes as support in heterogeneous catalysis were made very recently.[18] Yet, the situation is far not satisfying. In this letter, we report a theoretical prediction on viable sidewall oxidation and complexation of SWNTs by base-catalyzed [2+3] cycloaddition of transition metal oxide (OsO_4). Sidewall complexation of carbon nanotubes by transition metals and their complexes should be of great significance, as it can be a good starting point for further

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Scheme 1. [2+3] Cycloaddition between Alkene and OsO_4

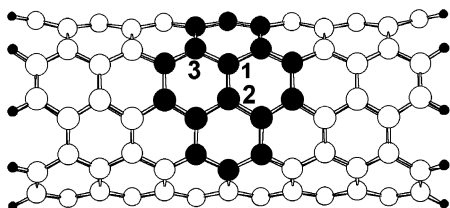functionalization and crystallization of carbon nanotubes, catalytic applications, and so on.

Transition metal oxides, e.g., OsO_4 and MnO_4^-, with metal-oxo groups were long known to be powerful oxidants in the oxidation of alkenes.[20] Among them, OsO_4 is known to be the most powerful, e.g., the base-catalyzed osmylation of alkenes occurs readily at low temperatures and produces osmate ester (see Scheme 1), further hydration of which results in diols.[20,21] Analogous reaction was found to occur readily with fullerenes, giving birth to the first exohedral fullerene−metal complex single crystal.[22] Inspired by these chemical precedents, one infers that similar process may proceed on the sidewalls of carbon nanotubes. Such an inference has been confirmed by our hybrid QM/MM (quantum chemistry/molecular mechanics) calculations reported herein.

We took the armchair (5,5) SWNT (optimal diameter ~6.8 Å) as an example and used a 2-layered ONIOM approach[23] to investigate the mechanism of the base-catalyzed [2+3] addition of OsO_4 onto the nanotube sidewall. For the two-layered ONIOM approach, the UFF (universal force field) method[24] and the hybrid density functional B3LYP method[25,26] in conjunction with effective core potential LANL2DZ basis set were employed for the low-level and high-level treat-

Figure 1. Fragment of (5,5) SWNT, in which the sixteen shaded atoms are used for the high-level treatment in the two-layered ONIOM (B3LYP:UFF) calculations.

ments, respectively. Geometry optimizations were performed within such a two-layered ONIOM (B3LYP/LANL-2DZ:UFF) approach using the Gaussian 98 program.[27] The B3LYP/LANL2DZ model chemistry was used previously to elucidate the mechanism of the amine-catalyzed (OsO_4 + C_2H_4) reaction.[21b] Figure 1 depicts a $C_{130}H_{20}$ tube modeling an armchair (5,5) SWNT (optimal diameter ∼6.8 Å), in which the high-level part is a C_{16} cluster (see the shaded atoms) in together with ten H atoms as boundary atoms. A similar modeling scheme was employed successfully in our previous study of the 1,3-dipolar cycloadditions[17,28] and Diels−Alder reactions[28] on the sidewall of (5,5) SWNT and by other groups in the theoretical studies of carbon nanotube chemistry.[29] Of the two inequivalent types of C−C pair sites, i.e., the 1,2 pair site and the 1,3 pair site (Figure 1), on the (5,5) SWNT, only the 1,2 pair site is considered in the present work, as it was found to be more ene-like than the 1,3-pair site.[17]

Figure 2 depicts the [2+3] cycloaddition products of OsO_4 onto the 1,2-pair site, either noncatalyzed (**LM1**) or catalyzed by one or two base (NH_3) molecules (**LM2** and **LM3**). The base-free (OsO_4 + SWNT) reaction is predicted to be endothermic by 9.6 kcal/mol at the ONIOM (B3LYP:UFF) level of theory. Therefore, this reaction is far less favorable over its molecular analogue between OsO_4 and ethylene, which was found to be considerably exothermic.[21] The results demonstrate the high chemical stability of the graphene-like structure of the SWNT sidewall. So far as an NH_3 molecule is involved, the OsO_4 + SWNT reaction becomes exothermic by 11.2 kcal/mol. By involving two NH_3 molecules, the reaction becomes exothermic by 29.1 kcal/mol. This reveals the stability of the as-formed osmate ester adduct (**LM3**) on the nanotube sidewall.

Furthermore, the transition state (**TS**) for the base-catalyzed reaction was optimized at the same level of theory and is depicted in Figure 2d. The calculations revealed that **TS** is by 15.8 kcal/mol lower in energy than free reactants. This is reasonable as OsO_4 itself can form complex with the base molecules[21] before attaching onto the nanotube sidewall. Indeed, the formation of the OsO_4·$2NH_3$ complex from OsO_4 and NH_3 is predicted to be exothermic by 26.5 kcal/mol at the B3LYP/LanL2DZ level of theory. Nevertheless, the prediction that **TS** is lower than free reactants in energy suggests that the base-catalyzed [2+3] cycloaddition of OsO_4 onto the nanotube sidewall is kinetically favorable. The geometry of the transition state depicted in Figure 2 indicates that the reaction proceeds in a concerted pathway.

$\Delta E= +9.6(+14.2)$
a) LM1

$\Delta E= -11.2(-6.4)$
b) LM2

$\Delta E= -29.1(-24.1)$
c) LM3

$\Delta E= -15.8(-12.1)$
d) TS
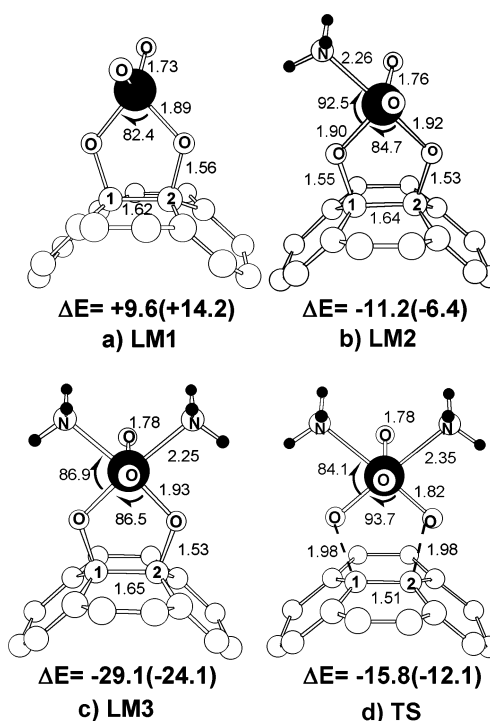
Figure 2. Optimized geometries (local views) of products for the base-free (a) and base-catalyzed (b and c) [3+2] cycloaddition of OsO_4 onto the sidewall of (5,5) SWNT as well as the transition state (d) for the base-catalyzed reaction. Relative energies (units in kcal/mol) calculated at the ONIOM (B3LYP/LANL2DZ:UFF) level are also given. (Relative energies given in parentheses were obtained at the B3LYP/LANL2DZ level with only the QM part being considered.)

As it is generally accepted that the reactivity of the sidewalls of carbon nanotubes depends largely on the tube wall curvature and the larger nanotubes would be less reactive,[30] one would expect similar sidewall reactivity toward the base-catalyzed osmylation for other SWNTs with curvatures similar to that of the SWNT(5,5), e.g, the zigzag (9,0) nanotubes. Nonetheless, further theoretical work is under way to see in what manner the title reaction would depend on the helicity and diameters of SWNTs.

Though the above calculations showed clearly the viability of sidewall complexation by base-catalyzed osmylation, one should add that the osmylation would occur first at the end caps of closed carbon nanotubes, which are fullerene-like, or at the open ends of carbon nanotubes, which are polycyclic aromatic-like. Both polycyclic aromatics and fullerenes were known to be subject to base-catalyzed osmylation.[22,31] Nevertheless, the sidewall complexation should proceed when these more active sites are consumed. The as-formed osmate ester species on the nanotube sidewall should be subject to further hydration, which produces hydroxyl groups on the sidewall. Further functionalization based on the hydroxyl groups should be much easier than the direct functionalization of the defect-free, graphene-like sidewalls of carbon nanotubes. As such, the as-osmylated nanotube sidewall can be a good starting point for further functionalization.

In summary, we predicted viable oxidation and complexation of the sidewalls of single-wall carbon nanotubes by

base-catalyzed [2+3] cycloaddition of transition metal oxide, OsO_4. The present study provides another example that the stable sidewalls of carbon nanotubes can be functionalized by means of synthetic organic chemistry. We believe the osmylation of nanotube sidewalls offers high flexibility for further functionalization. More significantly, the transition-metal complexation on the sidewalls of carbon nanotubes provides the basis not only for the preparation of nanotube-supported catalysts but also for the possibility of self-assembly of nanotubes with tailorable electronic properties that are important for advances in molecular electronics. We look forward to experimental realization of the reaction predicted herein as well as the potential applications of the as-functionalized carbon nanotubes.

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