Mini-Reviews in Organic Chemistry, 2008, *5*, 287-294

Cycloaddition and Complexation of Transition Metal Oxides with Materials Featuring an Analogous Bonding Motif: Alkenes, Diamond (100), Fullerene and Carbon Nanotubes

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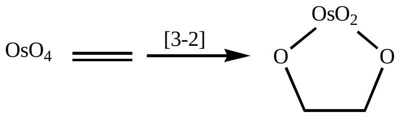
Abstract: In this review, the organic cycloaddition and complexation of transition metal oxides with alkene, diamond (100), fullerene and carbon nanotube have been summarized. A clear scenario that analogous chemistry reaction is able to occur in materials featuring an analogous bonding motif has been obtained. In particular, it is demonstrated that theoretical predictions can be employed as a very useful tool to provide experiments with potentially guided information. RuO_4 is proposed to be a better candidate than OsO_4 for investigating the cycloaddition of transition metal oxides with fullerene and carbon nanotube. In perspective, the typical organic cycloaddition and complexation of transition metal oxides with alkenes in organic chemistry could be extended to functionalize other structure-like substances including Si (100), Ge (100), disilene, digermene, silene and germene.

Keywords: Cycloaddition, transition metal oxides, alkene, diamond (100), fullerene, carbon nanotube, theoretical predictions.

INTRODUCTION

The cycloaddition and complexation of alkenes with osmium tetraoxide (OsO_4) at low temperature, namely osmylation of alkenes, which produces osmate ester and diols by further hydration, represents a prominent paradigm for transition-metal-mediated oxygen transfer reactions in organic chemistry, and its catalytic asymmetric form has proven to be a powerful method for enantioselective synthesis [1-3]. However, the fundamental mechanism of the addition of osmium tetraoxide to C=C bonds of alkenes, which is the initial step in the osmium-catalyzed cis-dihydroxylation of alkenes, remained unclear for several decades despite of the wide use of cis-dihydroxylation reaction in state-of-the-art chemical synthesis [4]. In this regard, it should be particularly pointed out that the controversy on the reaction mechanism of the addition of OsO_4 to alkenes was finally elucidated with the help of modern quantum chemical methods [5-7]. Theoretical results showed that the activation energy of the [2+2] addition is very high (>39kcal/mol), whereas the activation energy for the [3+2] addition is much smaller (<10kcal/mol), suggesting that the reaction follows the concerted [3+2] mechanism as shown in Scheme **1**. Later, a detailed comparison between computed data and measured kinetic isotope effects corroborated the concerted reaction route for the addition of OsO_4 to alkenes [8].



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

Nowadays, computational modeling is becoming an important tool for investigating topics in chemistry, including clarification of reaction mechanisms and predictions of the feasibility of chemical reactions that have not experimentally been realized. Consequently, a joint experimental and theoretical study will prompt us to shed light on many issues in chemistry with significantly improved efficiency and accuracy. In this short review, we will summarize the research progress on the cycloaddition and complexation of transition metal oxides, e.g., OsO_4 and RuO_4, with the diamond (100) surface, fullerene and carbon nanotube that are the materials featuring an analogous bonding motif to alkenes. In particular, we will demonstrate how experiment and theory advance each other to extend the classical reaction of oslymation of alkenes to the organic functionalization of solid materials. In many cases, theoretical predictions can offer experiment instructive information. The ultimate scenario summarized from experiment and theoretical prediction can be outlined in Scheme **2**.

1. CYCLOADDITION OF TRANSITION METAL OXIDES ONTO DIAMOND (100)

Diamond has been attracting considerable interest and attention as one of the most promising candidates for a wide variety of applications because of its fascinating and unique combination of mechanical, electrical, thermal and optical properties, for example, extreme hardness, large band gap, biocompatibility, high breakdown voltage, and ability to have a negative electron affinity [9-14]. The organic functionalization of diamond surface can be potentially useful to tailor its properties for specific applications [15-27]. By tuning the nature of organic functional groups attached to the diamond surface, new functions will be introduced to the matrix of diamond. Many typical reactions in organic chemistry have successfully been employed to functionalize the diamond (100) surface, e.g. Diels-Alder reactions and 1,3-dipolar cycloadditions [23-27]. The pioneering research work has clearly demonstrated the feasibility of functionalization of diamond (100) surface by means of synthetic organic chemistry and the diamond (100) surface can be regarded as “a big and highly reactive molecular alkene”. However, it should be noted that the cycloaddition and complexation of diamond (100) surface with transition metal oxides have not been reported experimentally. From the viewpoint of theory and chemical intuition, the typical osmylation of alkenes with OsO_4 in organic chemistry could be extended to functionalize the diamond (100) surface. This inference has been confirmed by our recent theoretical study [28]. The reaction profile, predicted by density functional theory coupled with a C_9H_{12} cluster model, for the cycloaddition of OsO_4 to the surface C=C dimer of diamond (100) is summarized in Fig. (**1**). Such a modeling method has successfully been used in our theoretical studies of the additions of carbenes and nitrenes onto diamond (100) [29-32], the epoxidation of diamond (100) with dioxiranes [33], the Diels-Alder reaction occurred on diamond (100) and the additions of 1,3-dipolar molecules onto diamond (100) [23-27]. Quite interestingly, it has been found that the [2+2] and [3+2] addition pathways can both possibly exist on diamond (100), particularly for the base-catalyzed process. The optimized geometries and transition states are depicted in Figs. (**2**) and (**3**).

The [3+2] addition pathway of OsO_4 onto C (100), leading to the product LM2, is predicted to be barrierless and highly exothermic by -85.4 kcal/mol. The exothermicity of osmylation of OsO_4 with C (100) is much higher than that of ethylene [4-7]. This is because of the higher reactivity of the surface C=C dimer than the C=C double

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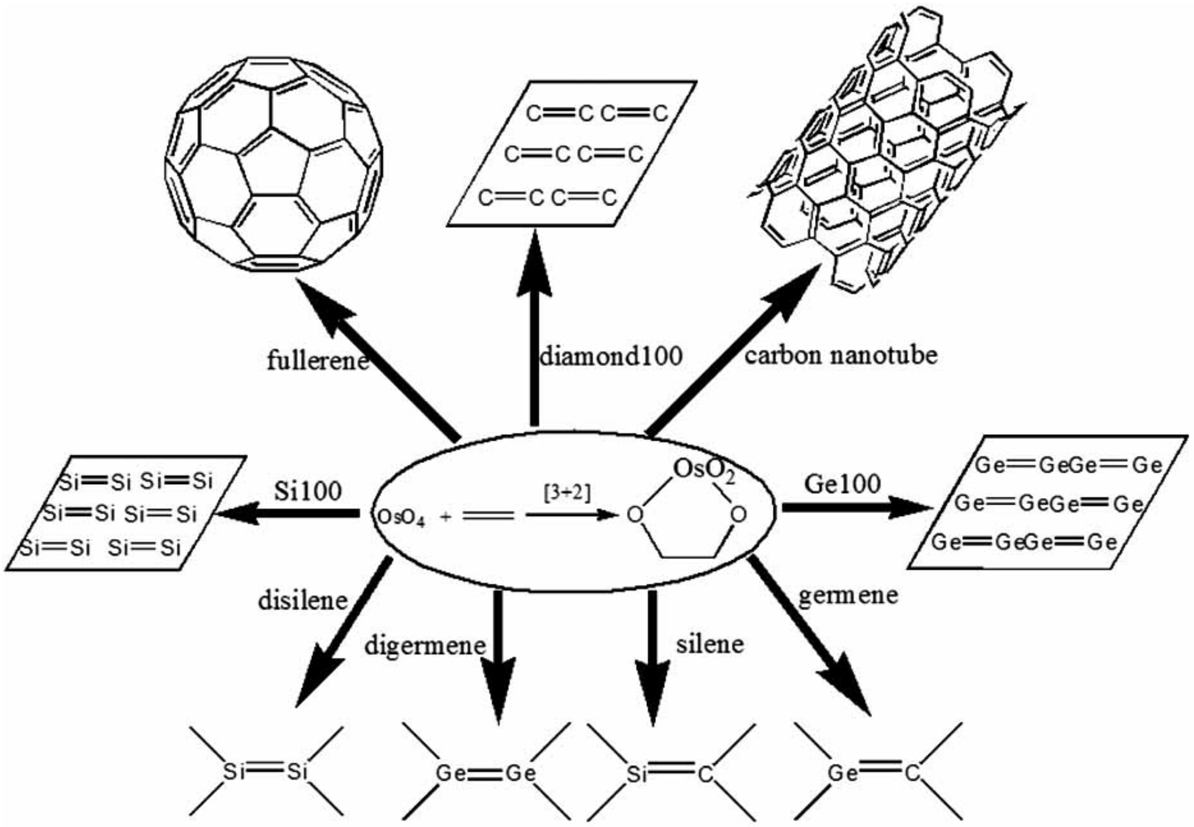


Scheme 2. Extension of classical osmylation of alkenes in organic chemistry to functionalize organic/inorgamic substances featuring an analogous bonding motif to alkenes.

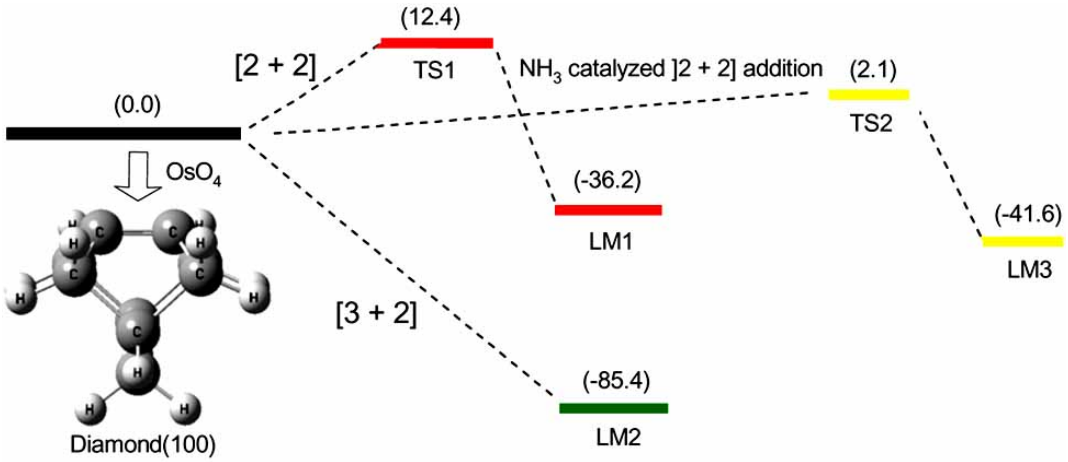


Fig. (1). Reaction pathways predicted at B3LYP/6-31G(d) theory using a C_9H_{12} cluster model. Reaction energies (units in kcal/mol) are given in parenthesis.

bond of ethylene, owing to the reduced overlap between the p orbitals of the surface C=C dimer of C (100). When the base NH_3 is used as a catalyst, the [3+2] addition of OsO_4 onto C (100) becomes more favorable. Fig. (**3**) shows the optimized geometries of LM4 and LM5, corresponding to one NH_3-catalyzed and two NH_3-catalyzed osmylation process, respectively. Clearly, as a NH_3 molecule is involved, the osmylation of OsO_4 with C (100) becomes more exothermic by -104.3 kcal/mol. By involving two NH_3 molecules, the exothermicity of the osmylation reaction is further increased to -118.2 kcal/mol.

Regarding the [2+2] addition pathway, it is predicted to be exothermic by –36.2 kcal/mol, together with an activation energy barrier of 12.4 kcal/mol. Interestingly, the activation energy of a NH_3 catalyzed [2+2] addition of OsO_4 onto C (100) is remarkably decreased to be 2.1 kcal/mol, along with the larger exothermicity of 41.6 kcal/mol. This strongly suggests that the [2+2] addition pathway is viable for the osmylation of OsO_4 with C (100). In distinct contrast, the osmylation of ethylene with OsO_4 can not involve a [2+2] addition pathway whether it is base-free or base-assisted [4-7]. For example, at the same level of theory, the activation energy barrier for the [2+2] addition of OsO_4 to ethylene is predicted to be 44.8 kcal/mol, in agreement with 43.3 kcal/mol in previous theoretical study. With two NH_3 molecules involved, the four membered intermediate would require a seven-coordinated metal atom, and a [2+2] addition mechanism is not possible [5-7]. As such, our theoretical results strongly illustrate that the [2+2] and [3+2] addition pathways for the osmylation of OsO_4 with the C (100) surface can both possibly exist, particularly for the base-catalyzed process.

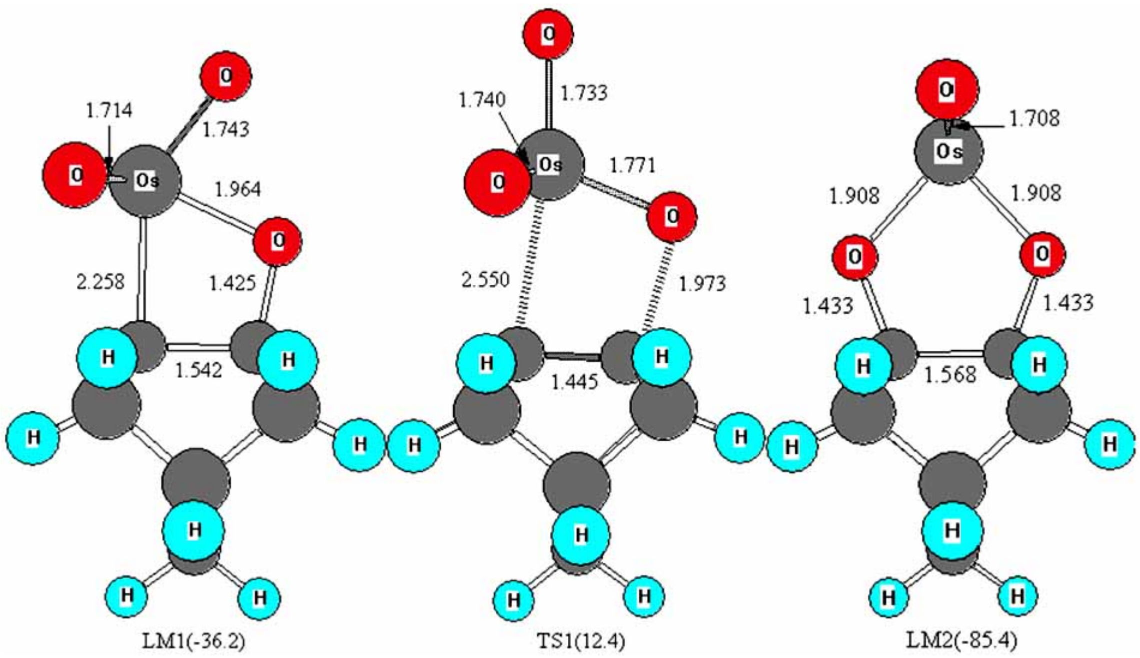


Fig. (2). Optimized geometries (units in Å for bond length) of the transition state and product for the base-free [2+2] and [3+2] addition of OsO_4 onto the C (100) surface, respectively. Reaction energies (units in kcal/mol) are given in parenthesis.

2. CYCLOADDITION OF TRANSITION METAL OXIDES ONTO FULLERENE

The chemical functionalization of fullerene C_{60}, or self-assembly surrounding the C_{60} cage, is an elegant way for tailoring their properties for specific applications. It is well documented that many well-known typical reactions for olefins in organic chemistry have been adopted to modify fullerenes and, in particular, the as-modified derivatives of C_{60} are able to have fascinating photonic, electronic, magnetic and biomedical properties that are useful for a wide range of potential applications [34-51].

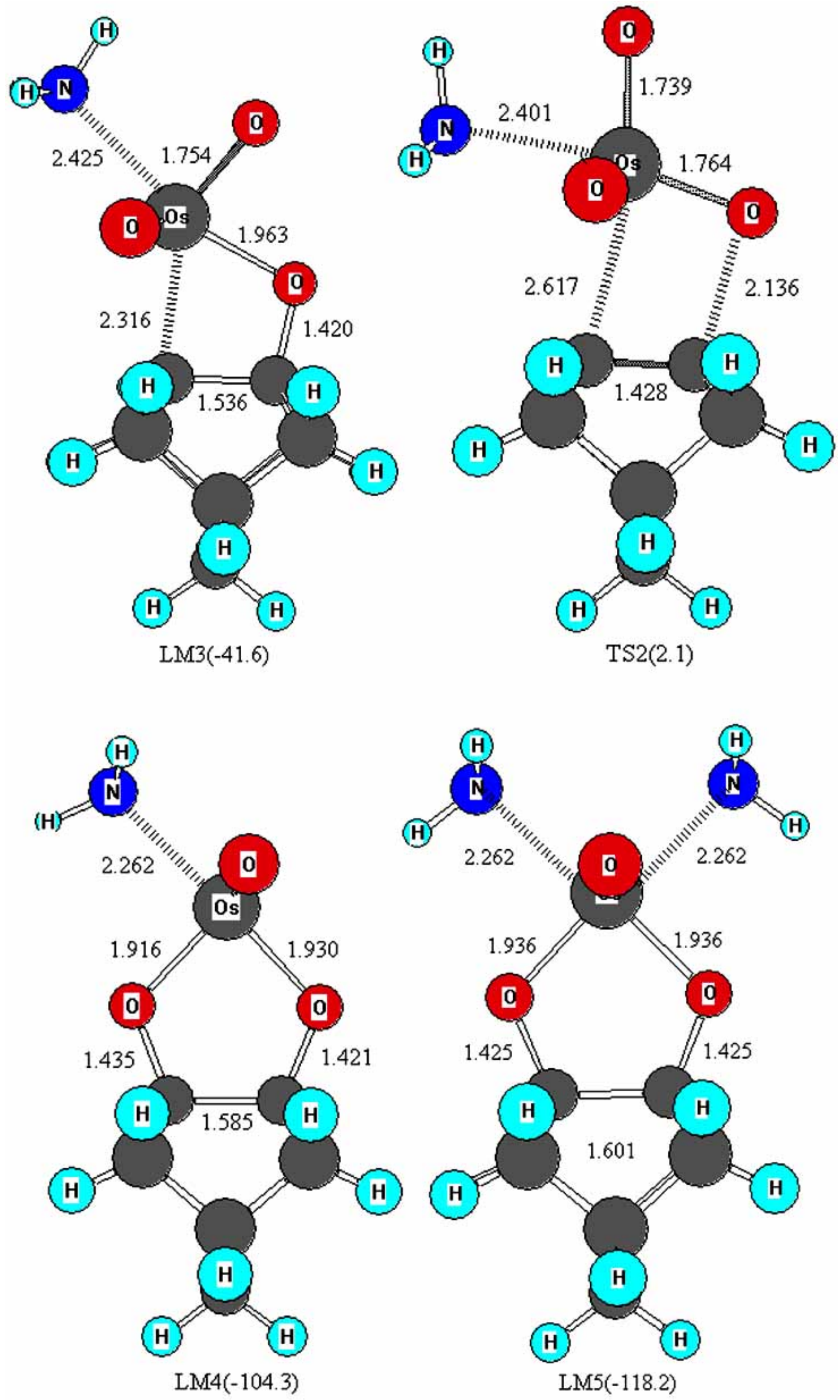
A central aspect of fullerene C_{60} is its functionalization by complexation and oxidation with transition metal oxides, because transition-metal complexes of fullerene are expected to be novel materials that offer significant potential for catalytic applications and crystallization, and so forth [52-57]. The typical addition of OsO_4 to alkene in organic chemistry has successfully been extended to functionalize C_{60}. The osmylation of C_{60} with OsO_4, in the presence of organic base, gave birth to the first pure fullerene-metal complex single crystal, $C_{60}(OsO_4)(4\text{-tert-butylpyridine})_2$ [52]. Osmylation has been used to grow single crystals of C_{60} for structure elucidation and achieve kinetic resolution of chiral fullerenes [52-56]. Moreover, osmylation offers the advantages of rapid as well as selective addition to C_{60}, which allows tailoring properties for construction of C_{60}-based novel materials.

Theoretical results on the addition of OsO_4 to C_{60} are in full agreement with experimental results. To simulate the additions of OsO_4 to C_{60}, the B3LYP method, which is a combination of HF with a DFT based on the Becke three-parameter exchange coupled with the Lee-Yang-Parr (LYP) correlation potential, has been used in our calculations. For C, O and H atoms, the standard all-electron split valence 6-31G(d) basis set was used while the effective core potential (ECP) of the LANL2DZ basis set was used for transition metal atoms. Using this theoretical approach, the calculated bond lengths of C_{60} are 1.40 and 1.45Å for the double bond C1-C2 and single bond C2-C3 respectively (Fig. **4**), which are in excellent agreement with experimental values (single bond 1.46 Å; double bond 1.40 Å) [58].

Fig. (**5**) displays the optimized geometries and calculated reaction energies regarding the base-free and base-catalyzed additions of OsO_4 onto the C1-C2 double bond of C_{60}, respectively. Obviously, the addition reaction of OsO_4 onto the C1-C2 of C_{60} is endothermic by +21.4 kcal/mol, meaning that the as-formed C_{60}-OsO_4 complex is thermodynamically unfavorable. With the organic base pyridine involved, the addition reaction will become exothermic by -9.1 kcal/mol. When the stronger base NH_3 than pyridine is used to simulate the base-catalyzed addition reaction, the exothermicity is further increased to -14.3 kcal/mol. Thus, the calculated results by density functional theory indicate the addition and complexation of OsO_4 with C_{60} needs the presence of base as a catalyst, which is in full agreement with experimental results [52-56]. Meanwhile, the addition of OsO_4 onto the C2-C3 single bond of C_{60} has also been studied theoretically. The calculated reaction energies are +36.2 kcal/mol and +8.4 kcal/mol for the base-free and NH_3-catalyzed addition reaction, respectively, suggesting the addition of OsO_4 onto the C2-C3 single bond of C_{60} is thermodynamically unfavorable. Therefore, the addition of OsO_4 onto C_{60} is a regioselective process, which is in faithful accordance with the results from experiment [54].

In organic chemistry, ruthenium tetraoxide (RuO_4) is a transition metal oxide with a much more vigorous oxidation capability than other transition metal oxides, such as OsO_4, MnO_4^- and ReO_4^- [59,60]. In fact, Ru-based oxidation catalysis has become increasingly important owing to the unique properties of this special transition metal, ranging from the powerful detoxification oxidations to the oxidative conversion of water to O_2 and the elegant hydroxylation of olefins [61]. Since RuO_4 is much more powerful as an oxidant than OsO_4, it can be naturally envisaged that the oxidation and complexation of RuO_4 with C_{60} should be more facile than that of OsO4; this process could readily occur without the presence of organic base as a catalyst. Such an inference has been verified by our theoretical calculations. Note that the addition of RuO_4 onto fullerenes has not been reported experimentally so far.

Fig. (**6**) shows the optimized geometries and calculated reaction energies for the addition of RuO_4 onto C_{60}. Clearly, the addition of RuO_4 onto C_{60} does not need the presence of organic base as a catalyst because the base-free addition of RuO_4 onto the C1-C2 double bond of C_{60} is thermodynamically favorable by -13.6 kcal/mol, which is markedly different from the case of OsO_4. This reflects the more powerful oxidation capability of RuO_4 than OsO_4. Meanwhile, the



LM3(-41.6) TS2(2.1)

LM4(-104.3) LM5(-118.2)

Fig. (3). Optimized geometries (units in Å for bond length) of the transition state and product for the base-catalyzed [2+2] and [3+2] addition of OsO_4 onto the C (100) surface, respectively. Reaction energies (units in kcal/mol) are given in parenthesis.

addition of RuO_4 onto the C2-C3 single bond of C_{60} has also been studied, for which the calculated reaction energy is +3.7 kcal/mol, suggesting that the base-free addition of RuO_4 onto C_{60} also shows a regioselectivity. Therefore, as compared to OsO_4 for osmylation of C_{60}, RuO_4 can be used as an alternative but regioselective and more powerful oxidant for the oxidation and complexation of C_{60}.

On the other hand, it should be noted that, if the base is involved, the addition reaction will become more exothermic as well. For example, the pyridine-catalyzed and NH_3-catalyzed additions of RuO_4 onto the C1-C2 of C_{60} are exothermic by -16.3 and -42.4 kcal/mol, respectively. This indicates that the functionality resulting from the additions of OsO_4 and RuO_4 onto C_{60} can be controlled by the ligand on osmium and ruthenium. Experiments showed that the ligand on osmium can be chosen to cause the osmylated-C_{60} adduct to precipitate and protect it from further reaction [54]. Until now, the addition and complexation of RuO_4 with C_{60} have not been reported experi-

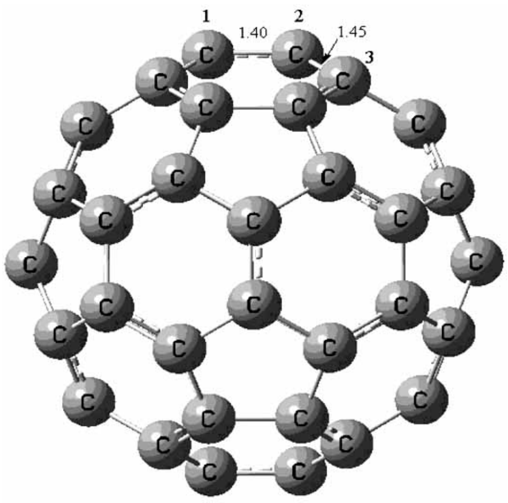


Fig. (4). Optimized geometries (units in Ǻ for bond length) of C_{60}.

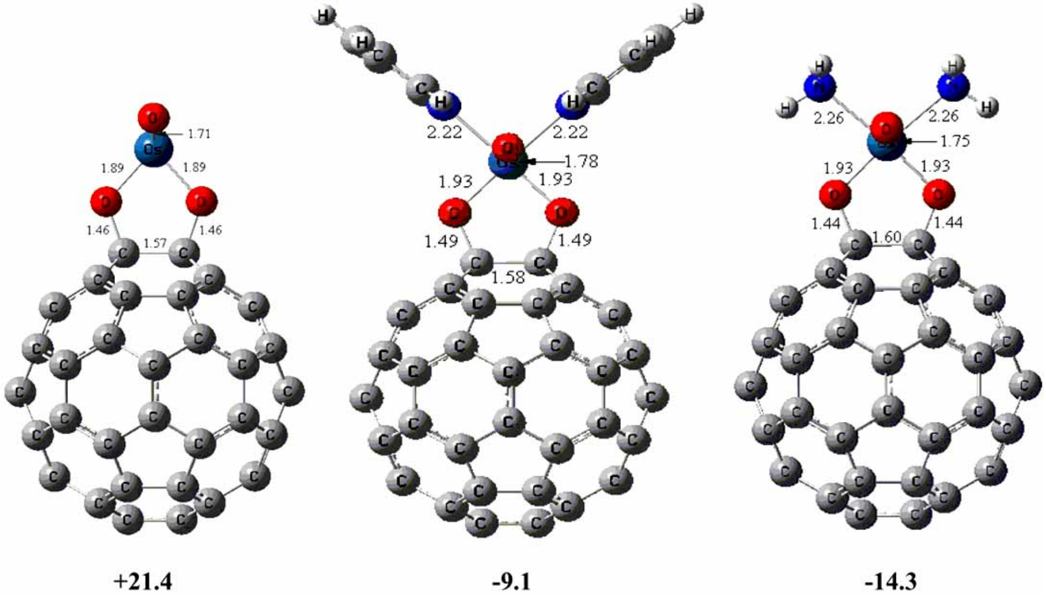


Fig. (5). Optimized geometries (units in Ǻ for bond length) and calculated reaction energies (units in kcal/mol) for the addition of OsO_4 onto the C1-C2 double bond of C_{60}.

mentally. It is hoped that our theoretical results would provide experiment with guided information and stimulate more interest into this research topic.

3. CYCLOADDITION OF TRANSITION METAL OXIDES ONTO CARBON NANOTUBE

As mentioned above, osmylation of fullerenes has been well understood both experimentally and theoretically. However, osmylation of carbon nanotubes seems more complex [62-65]. Inspired by the chemical precedents of successful extension of osmylation of alkenes to functionalize fullerenes, Lu *et al.* firstly predicted, by means of a two-layered ONIOM approach, that the gas-phase [3+2] addition of OsO_4 to the sidewall of carbon nanotube could be viable in the presence of base as a catalyst [62], as shown in Scheme **3** and Fig. (**7**).

Since there is significant interest on the chemical modification of carbon nanotubes, this theoretical prediction immediately triggered the attention from experimentalists. It was reported that the sidewall osmylation of single walled carbon nanotubes with the use of OsO_4 could be approached by UV irradiation in the presence of oxygen, which leads to an increase in electrical resistance for carbon nanotube [63]. The authors interpreted this phenomenon as arising from covalent functionalization of cycloaddition of OsO_4 to the sidewall of carbon nanotube. However, conductivity measurements alone are insufficient evidence for the presence of a covalent linkage. Without more extensive structural characterization, the precise chemical nature of OsO_4-nanotube interaction can not be established. Also, this speculated explanation was not supported by the previous theoretical calculation [62]. Although the theoretical prediction by Lu *et al.* has not been confirmed experimentally, it provides experiments with guided information ant thus advance experimentalists to investigate this important chemical reaction on the sidewall of carbon nanotubes that would be a good starting point for further functionalization. Due to the high stability of graphene-like sidewall of carbon nanotubes, the interaction of OsO_4 with carbon nanotubes is weak, which may be the reason why the gas-phase osmylation of carbon nanotubes has not been realized experimentally until now. We think that an alternative transition metal oxide with much more powerful oxidant capability than OsO_4 should be chosen for investigating transition metal oxide-nanotube interactions, which may reconcile the inconsistency between theory and experiment. This issue will be addressed in the following.

Whereas, the comprehensive experimental investigation on understanding the photo- promoted osmylation of single walled carbon nantoubes has been reported in a solution phase [64]. It was showed that such a solution-phase photo-reaction occurs selectively with metallic single walled carbon nanotubes in the presence of oxygen and UV irradiation, leading predominantly to thickly coated carbon nanotubes densely covered with OsO_2.

Considering the much more powerful oxidant capability of RuO_4 than OsO_4, we propose that RuO_4 can potentially be used as a better candidate to investigate the addition and complexation of transition metal oxides with the sidewall of carbon nanotube. We have used theoretical simulations to confirm this inference. The calculated results demonstrate that the addition and complexation of RuO_4 with the sidewall of carbon nanotube are quite thermodynamically favorable without the base as a catalyst, which is in great contrast to that of OsO_4. A $C_{130}H_{20}$ model along with DFT/B3LYP method was used in our simulations, as depicted in Fig. (**8**). For C, H, O and Ru atoms, the basis set of LANL2DZ was adoped. Similar to previous theoreti-

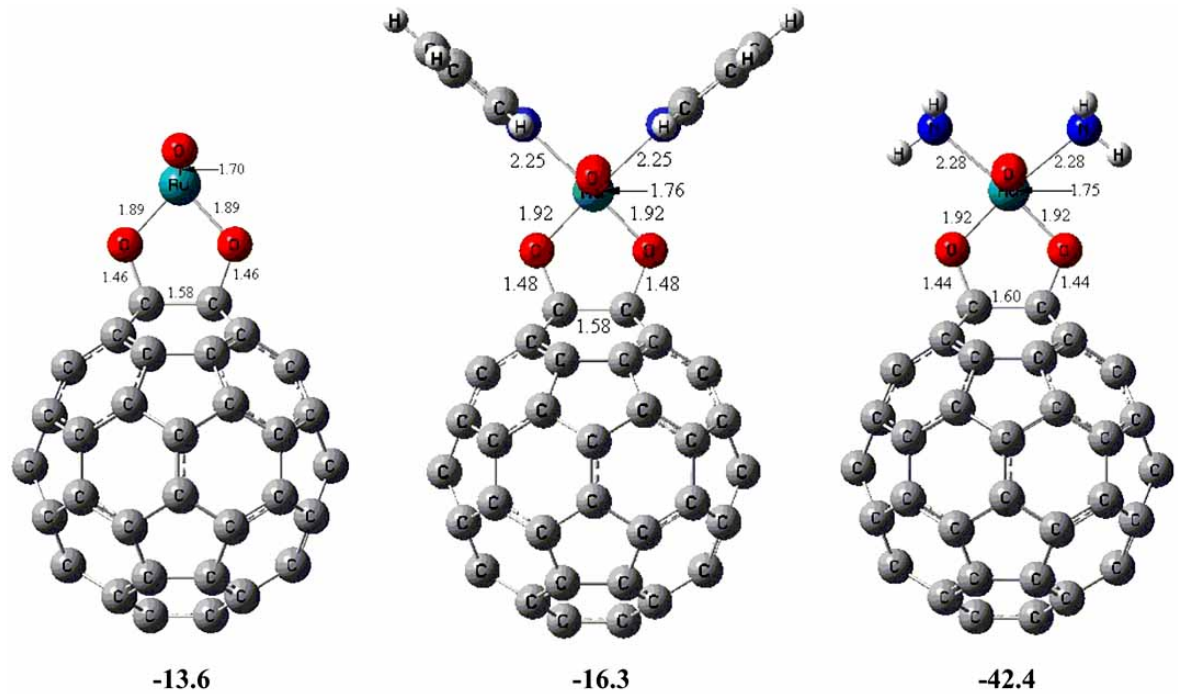
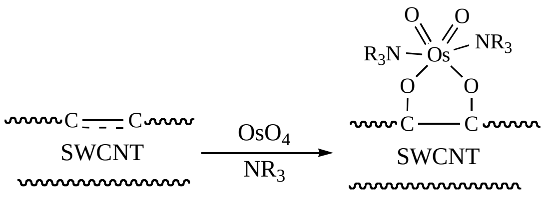


Fig. (6). Optimized geometries (units in Å for bond length) and calculated reaction energies (units in kcal/mol) for the addition of RuO_4 onto the C1-C2 double bond of C_{60}.



Scheme 3. Osmylation of the sidewall of carbon nanotube predicted by the ONIOM method.

cal work, only the C1-C2 pair site was considered in our calculations because it was found to be more ethylene-like than the C1-C3 pair site. Also, our purpose is only to confirm the more powerful oxidant ability of RuO_4 than OsO_4 onto the sidewall of carbon nanotubes. The B3LYP/LANL2DZ model method was previously used to study the addition of transition metal oxides with alkenes [5]. The optimized geometries and calculated reaction energies have been shown in Fig. (**8**). The [3+2] addition of OsO_4 onto the sidewall of carbon nanotube is endothermic by +9.9 kcal/mol, indicating the reaction is thermodynamically unfavourable that is in line with previous theoretical prediction [62]. In contrast, the [3+2] addition of RuO_4 onto the sidewall of carbon nanotube is highly exothermic by -16.3 kcal/mol, which is higher than one-NH_3 catalyzed addition of OsO_4 onto the sidewall of carbon nanotube in previous theoretical prediction [62]. This is in faithful accordance with the more powerful oxidant capability of RuO_4 than OsO_4. Thus, we propose that RuO_4 can be used as an excellent candidate to investigate the interaction of transition metal oxides with carbon nanotubes in the gas phase.

SUMMARY AND PERSPECTIVE

The addition of transition metal oxides to alkenes is one of the most important reactions in organic chemistry. The typical osmylation of alkenes with OsO_4 has firstly been extended to functionalize fullerene C_{60}, giving birth to the first exohedral fullerene-metal complex single crystal. Our theoretical simulations have shown that osmylation of C_{60} with OsO_4 needs the presence of base as a catalyst, which is in faithful agreement with experiments. We also propose that the addition of RuO_4 onto fullerenes should be much more facile than that of OsO_4, owing to its more powerful oxidant capability than OsO_4.

The successful extension of traditional osmylation of alkenes with OsO_4 to modify fullerenes indicates that this important chemical reaction could also be applied to functionalize carbon nanotubes, namely the twin sister of fullerenes. In this respect, theory goes ahead of experiment. Theoretical predictions firstly demonstrates the viable oxidation and addition of the sidewall of carbon nanotubes with OsO_4, giving rise to osmate ester adducts on the nanotube sidewall. In particular, it was pointed out that the gas-phase addition reaction of OsO_4 onto the sidewall of carbon nanotubes requires catalysis by a base. Later, experimentalists reported that the sidewall osmylation of carbon nanotubes can be achieved by exposing the tubes to OsO_4 vapor under UV photo-irradiation. Based on the observed increase in the electrical resistance of carbon nanotubes, the authors speculated that the covalent osmate ester was formed on the sidewall of carbon nanotubes. This interpretation is not convincing since conductivity measurements alone are insufficient evidence for the presence of a covalent linkage. Although, regarding osmylation of carbon nanotubes, there is somewhat inconsistency between experiment and theory, it can be seen that these pioneering work suggests some of the challenges associated with the addition of OsO_4 onto the sidewall of carbon nanotubes, thus calling for more extensive work on this topic both experimentally and theoretically. On the other hand, we argue that RuO_4 could be used as a better candidate to investigate the interaction of transition metal oxides with the sidewall of carbon nanotubes because our theoretical simulations indicate the base-free addition of RuO_4 onto the sidewall of carbon nanotubes is quite exothermic, in distinct contrast to that of OsO_4. Thus, it is reasonable to believe that the gas-phase addition of RuO_4 onto the sidewall of carbon nanotube can occur without the presence of UV irradiation and oxygen. In this case, the comparison between experiment and theory would be simplified.

Diamond (100) is another allotrope of carbon and features the C=C dimer on the surface that is more reactive than ethylene, due to the reduced overlap of p orbitals. Of course, the surface C=C dimer of diamond (100) is much more reactive than that of fullerenes and car-

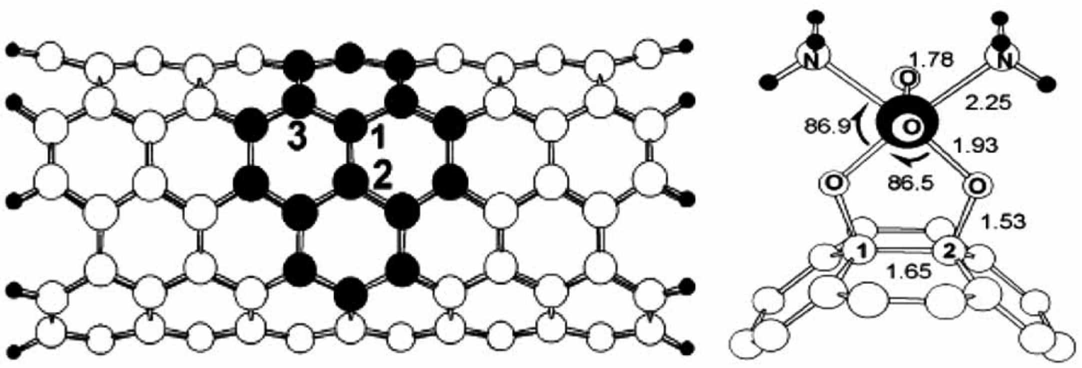


Fig. (7). The model and optimized geometry (units in Ǻ for bond length) of base-catalyzed osmylation of single walled carbon nanotube theoretically predicted using the ONIOM approach [62].

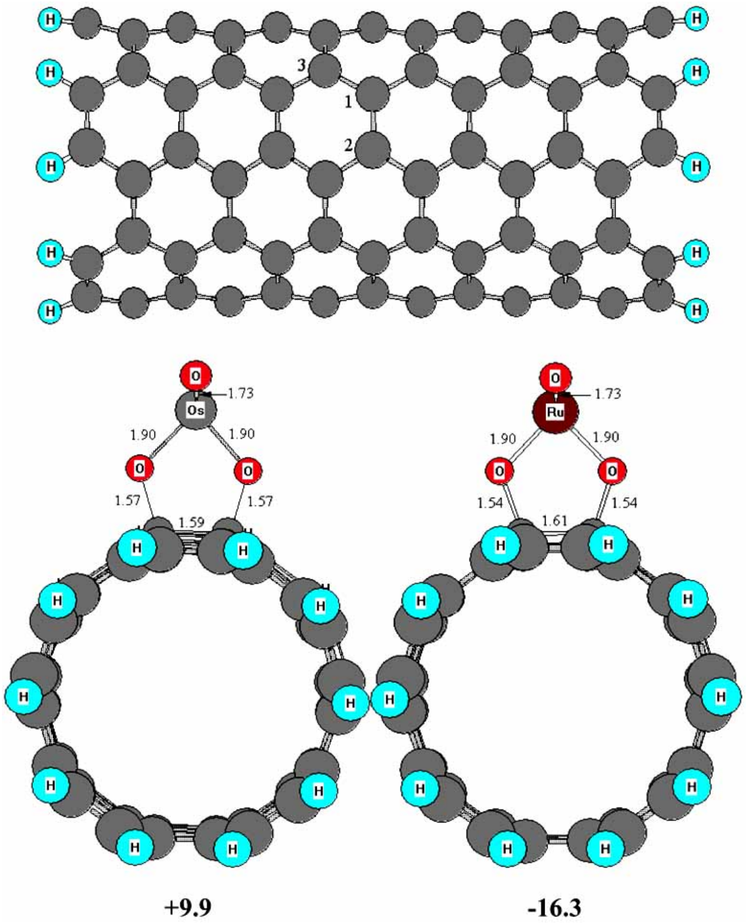


Fig. (8). The model and optimized geometry (units in Ǻ for bond length) and calculated reaction energies (units in kcal/mol) of [3+2] addition of OsO_4 and RuO_4 onto the sidewall of single walled carbon nanotube predicted using the B3LYP/LANL2DZ method.

bon nanotubes. Hence, by chemical intuition, it is natural to believe that osmylation of alkenes can also happen on the diamond (100) surface. Such an inference has been confirmed by our theoretical calculations. Interestingly, we have found that, owing to high reactivity of the surface C=C dimer of diamond (100), the [2+2] and [3+2] addition pathways of OsO_4 onto diamond (100) can both possibly exist, which is in remarkable contrast to osmylation of alkenes. We are looking forward to experimental realization of osmylation of diamond (100) with OsO_4 and potential applications of the as-functionalized diamond (100) surface.

Significantly, osmylation reaction provides an easy way for oxidation and modification of fullerenes, carbon nanotubes and diamond (100), and can be used as a starting point for further chemical manipulations. In addition, osmylation offers the preparation of fullerenes, nanotubes and diamond (100)-supported catalysts as well as the possibility of tailoring the chemical properties of these solid materials.

Disilenes, digermenes, silenes, germenes, Si (100) and Ge (100) feature an analogous bonding motif to that of ethylene, fullerene, carbon nanotube and diamond (100) [66-74]. Thus, it is reasonable in perspective that the addition reaction of transition metal oxides to alkenes, including osmylation of alkenes with OsO_4, can also be extended to modify these substances. This would open a new research branch in chemistry that is worthy of attracting interest from both experiment and theory. No doubt, research in this respect would add much to the richness of chemistry of solid surfaces and organic/inorganic chemistry, as well as reinforce the basic concept in chemistry that there is an intimate relationship between structure and reactivity. In fact, current chemistry mostly rest on the application of a well-known old reaction, and this has been clearly witnessed by the functionalization of fullerenes and carbon nanotubes using traditional organic/inorganic reactions during the past two decades. In this case, theoretical predictions can be a very useful tool to provide experiments with guided information, and shed light on reaction mechanisms. It goes without saying that today's chemistry is an intertwining discipline of combination of experimental and theoretical chemistry, and a joint theoretical and experimental study can advance each other, hence contributing to understanding and exploring chemistry issues efficiently and comprehensively.

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Received: March 10, 2008 **Revised: May 12, 2008** **Accepted: May 14, 2008**