

Predicting Facile Epoxidation of the Diamond (100) Surface by Dioxiranes and Subsequent Ring-Opening Reactions with Nucleophiles

Yi-Jun Xu,^{*,†} Yong-Fan Zhang,[‡] and Jun-Qian Li[‡]

School of Chemistry, Main Building, Cardiff University, Cardiff CF10 3AT, United Kingdom, and
Department of Chemistry, Fuzhou University, Fuzhou 350002, China

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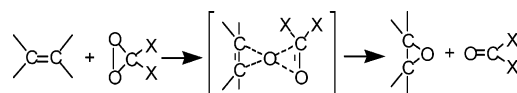
By means of density functional theory coupled with effective cluster models, we have theoretically predicted the viability of epoxidation of the diamond (100) surface by organic dioxiranes. In addition, subsequent ring-opening reactions of the as-formed epoxide surface species with some nucleophiles, including water, ammonia, and alcohol, have also been explored. The facile epoxidation of diamond (100) by dioxiranes presents a new alternative for oxidation of the diamond (100) surface. More importantly, the as-formed epoxide-like surface species would be a useful springboard for further functionalizations of the diamond surface given the well-known abundant chemistry of organic epoxides. Therefore, this approach provides another new route to chemical functionalization of the diamond surface, which is potentially useful for leading to the improvement of diamond behavior and constructing new hybrid diamond-based materials for wide potential applications in many fields. In perspective, implications for other theoretical work are also discussed.

1. Introduction

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.^{1–4} The chemical functionalization of the diamond surface can introduce new physical and chemical properties, thus leading to the improvement of its behavior for specific potential applications.⁵ For example, the hydrogen-terminated diamond surface is hydrophobic and p-type conducting, whereas the oxygen-terminated diamond surface is hydrophilic and insulating.^{5c} More interestingly, it was found that incorporation of nitrogen into the diamond lattice affects its thermal conductivity, optical transparency, hardness, and band gap.^{2,5m,n} Clearly then, the properties of the diamond surface intimately depend on the kind of species chemically bonded to the surface. In particular, recent developments in biotechnology and molecular electronics have further fueled the increased interest in chemical functionalization of solid surfaces.

Against this background, great effort has been directed toward seeking specific methods of achieving the chemical functionalization of the diamond surface both experimentally and theoretically.^{5–8} For instance, by means of density functional theory with effective cluster models, it was theoretically predicted that 1,3-dipolar cycloadditions of a series of 1,3-dipolar molecules onto the diamond (100) surface are much more favorable than their ethylene molecular analogues both thermodynamically and kinetically.^{6a,b} Similarly, another class of well-known Diels–Alder reactions on the diamond (100) surface has been theoretically investigated using cluster model calculations.^{6c,d} Apart from these efforts, most recently, we have

SCHEME 1: Epoxidation of Alkenes with Dioxiranes



predicted the viability that the C (100) surface can be chemically functionalized by the well-known addition reactions of carbenes and nitrenes to alkenes.^{7,8} More fascinating is the experimental work reported by Wang et al. and Hovis et al.,^{6e,f} who found that 1,3-butadiene can react with the C (100) surface to form a Diels–Alder adduct^{6e} and that the “symmetry-forbidden” [2 + 2] cycloaddition of cyclopentene with alkenes can occur on the C (100) surface,^{6f} respectively. These pioneering findings are quite encouraging and significant because they strongly demonstrate the feasibility of functionalizing diamond surfaces by means of synthetic organic chemistry.^{6–8} The diamond (100) surface can be vividly depicted as a “high reactive and big organic molecular alkene, but specifically has the biradical character in the surface C=C dimer”.^{6–8} Hence, many well-known reactions with respect to alkenes in organic chemistry can possibly be applied to the functionalized C (100) surface. Indeed, as is often the case with large steps forward in experimental techniques, current fundamentals mostly rest on the new application of an established well-known reaction. In this regard, theoretical computations can be very useful for predicting the unknown reaction and disclosing the possible reaction mechanism at the molecular level. At the same time, theory can provide instructive and valuable information for experiments.

Dioxiranes are three-membered ring, strained peroxides that can be considered as a paradigm reagent of electrophilic O-transfer reagents.⁹ In recent years, as highly powerful oxidants, dioxiranes have attracted considerable increasing popularity as oxygen-transfer reagents by synthetic chemists.⁹ An important application of dioxiranes is the epoxidation of alkenes (Scheme 1), with the so-formed epoxide being a very versatile intermediate for further organic transformations.¹⁰

* To whom correspondence should be addressed. E-mail: XuY7@cf.ac.uk.

[†] Cardiff University.

[‡] Fuzhou University.

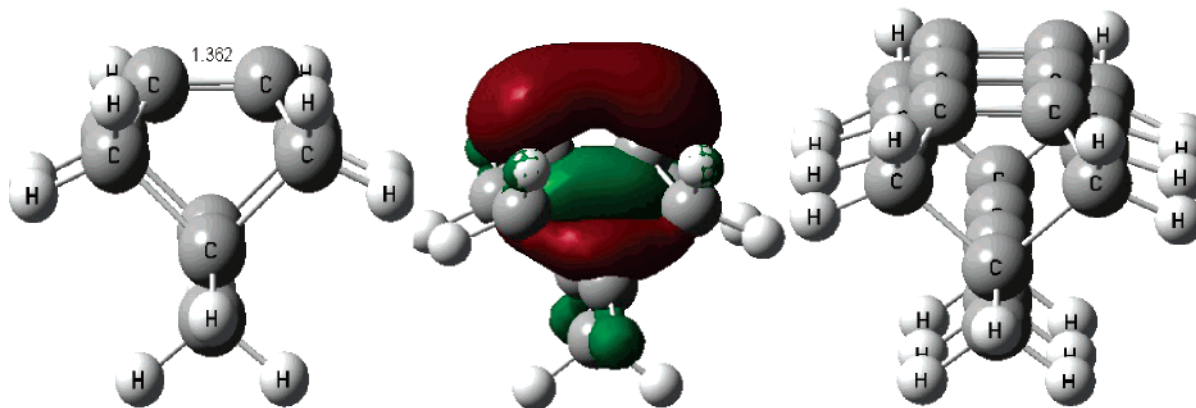


Figure 1. B3LYP/6-31G(d)-optimized geometries (units of Å for bond length) of C_9H_{12} and $C_{21}H_{20}$ clusters and highest occupied molecular orbital (HOMO) of the C_9H_{12} cluster.

Meanwhile, it is worth noting that the analogous chemical process has been reported regarding the epoxidation of dioxiranes with fullerene¹¹ and single-walled carbon nanotubes (SWNTs),¹² although possible ring-opening reactions were not considered. On the other hand, note that the reactivity of the surface dimer of C (100) is much higher than those of fullerene and SWNTs, which can be attributed to the high graphene-like π -conjugating bonding character.^{7,8,12} Therefore, analogous epoxidation of dioxiranes with the C (100) surface, another allotrope of carbon, should be expected.

The purpose of this article is two-fold: (a) to confirm the inference that the facile epoxidation of diamond (100) with dioxiranes is viable and (b) to further explore the possible ring-opening reaction pathways of the as-formed epoxide surface species with nucleophiles including water, ammonia, and methanol. The calculated results suggest that the epoxidation of diamond (100) not only can be used as a facile alternative for the oxidation of the diamond (100) surface, but also can offer a new route to the chemical functionalization of the diamond (100) surface.

2. Computational Details and Models

As has previously been done,^{6a-d,7,8} an effective C_9H_{12} cluster model was employed to represent a dimer site on the C (100)-2 \times 1 surface. The larger cluster model $C_{21}H_{20}$ was used to confirm the results obtained with the C_9H_{12} cluster (as shown in Figure 1). At the same time, the epoxidation of dioxiranes between two adjacent surface C=C dimers was also considered using the larger $C_{21}H_{20}$ cluster. This surface model was used in our recent theoretical predictions of the additions of carbenes and nitrenes to the C (100) surface.^{7,8} The same modeling scheme has also been used successfully by other research groups in theoretical studies of 1,3-polar cycloadditions^{6a,b} and Diels–Alder reactions^{6c,d} on the C (100) surface.

Theoretically, this surface model fulfills the requirements of the stoichiometry principle, the neutrality principle, and the coordination principle so that it can be concluded as a good model of choice.^{13e,i,k} In principle, cluster model calculations ought to be the most straightforward method to theoretically study surface processes in which the electronic properties are described in terms of local orbitals, allowing one to treat problems occurring on a solid surface with the typical language of chemistry, the language of orbitals.^{13b,j} Cluster model calculations tend to simulate single isolated adsorbed species in the low-surface-coverage regime, whereas slab calculations are better suited to model adsorbate overlayers and the substrate band structure at higher coverage. Objectively speaking, both

TABLE 1: Calculated Activation Energies (ΔE_a , kcal/mol) and Reaction Energies (ΔE_r , kcal/mol) for the Epoxidations of DO, DFDO, and MTFDO with the C (100)-2 \times 1 Surface

| system | method | ΔE_a | ΔE_r |
|------------------------|---------------------|-------------------|--------------|
| DO + C_9H_{12} | B3LYP/6-31G(d) | — | −79.4 |
| | B3LYP/6-311G(2d,2p) | — | −78.8 |
| DFDO + C_9H_{12} | B3LYP/6-31G(d) | — | −89.4 |
| | B3LYP/6-311G(2d,2p) | — | −88.5 |
| MTFDO + C_9H_{12} | B3LYP/6-31G(d) | — | −80.0 |
| | B3LYP/6-311G(2d,2p) | — | −78.8 |
| DO + $C_{21}H_{20}$ | B3LYP/6-31G(d) | — | −77.5 |
| | B3LYP/6-311G(2d,2p) | — | −77.0 |
| DFDO + $C_{21}H_{20}$ | B3LYP/6-31G(d) | — | −86.5 |
| | B3LYP/6-311G(2d,2p) | — | −85.4 |
| MTFDO + $C_{21}H_{20}$ | B3LYP/6-31G(d) | — | −76.1 |
| | B3LYP/6-311G(2d,2p) | — | −74.3 |
| DO + ethylene | B3LYP/6-31G(d) | 13.2 | −52.5 |
| DFDO + ethylene | B3LYP/6-31G(d) | −1.1 ^a | −62.4 |
| MTFDO + ethylene | B3LYP/6-31G(d) | 11.0 | −53.1 |

^a The activation energy predicted at the B3LYP/6-31G(d) level of theory should be −1.1 kcal/mol, not −0.1 kcal/mol reported in a previous study (ref 12).

methods have their respective advantages and can offer complementary information.^{13b,j} On the other hand, it is reasonable to use such a C_9H_{12} cluster to qualitatively predict the possibility of a given reaction because the surface dimer can be viewed as the most reactive site on the C (100)-2 \times 1 surface. Moreover, cluster models present advantages in terms of a compromise between accuracy and computational cost if clusters are properly selected.¹³

In this work, three kinds of model molecules were first selected, namely, dioxirane (DO), difluorodioxirane (DFDO), and methyl(trifluoromethyl)dioxirane (MTFDO), to assess whether they can undergo epoxidation with the C (100) surface. Subsequent possible ring-opening reactions of the as-formed surface epoxide species with nucleophiles, including water (H_2O), ammonia (NH_3), and methanol (CH_3OH), were also considered. The hybrid density functional B3LYP method,¹⁴ i.e., Becke's three-parameter nonlocal-exchange functional with the correlation functional of Lee–Yang–Parr, along with the standard all-electron split-valence 6-31G(d) basis set was employed. Recent encouraging studies have consistently reinforced the reliability of using this theoretical method to study surface reactions on the C (100)-2 \times 1 surface.^{6a-d,7,8} Geometry optimizations with no constrained degrees of freedom were carried out using analytical gradients and the Berny algorithm.¹⁵ At the B3LYP/6-31G(d) level of theory, geometry optimization shows that the C=C dimer in the C_9H_{12} cluster is symmetric, as can clearly be seen from the optimized geometry and the

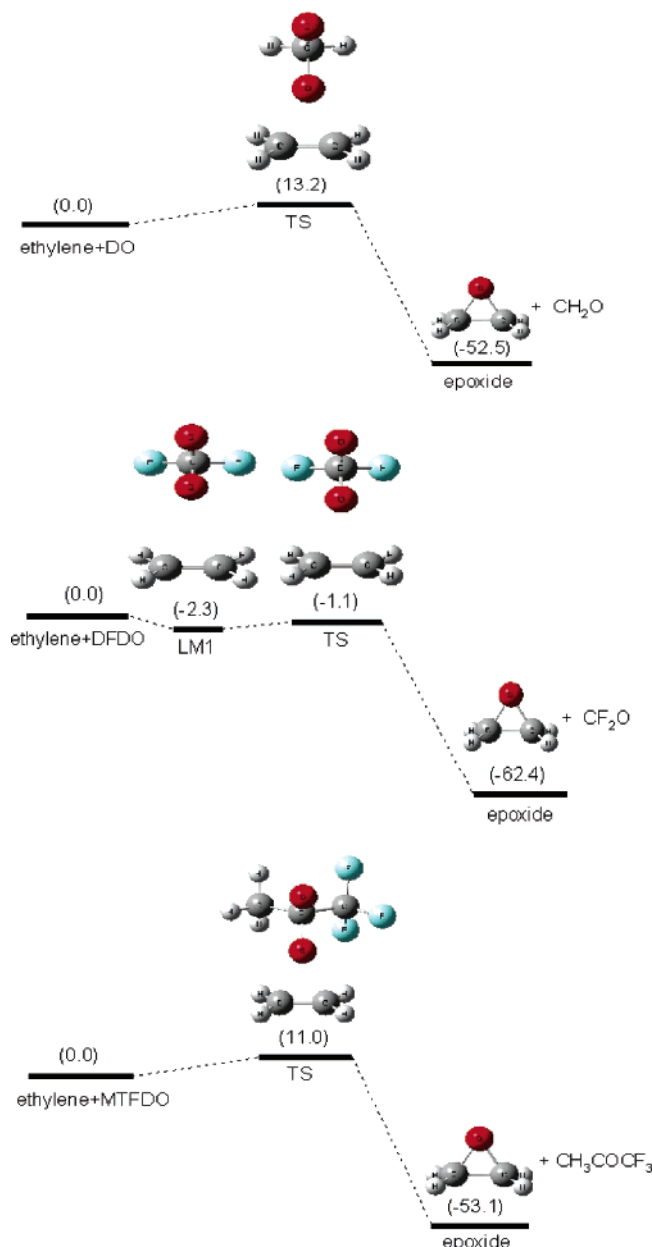


Figure 2. Theoretically calculated reaction profiles of ethylene with DO, DFDO, and MTFDO at the B3LYP/6-31G(d) level of theory.

highest occupied molecular orbital (HOMO) in Figure 1. This is in good agreement with the experimental observation.¹⁶ Single-point calculations were done, using the 6-311G(2d,2p) basis set, to investigate the effect of the basis set on the reaction energetics, although our main interest is in the qualitative trend, not in absolute energetics. These surface reactions were compared to those of the gas-phase ethylene molecular analogues and available data for SWNCTs in the literature. All calculations were performed with the Gaussian 98 program.¹⁵

3. Results and Discussion

Table 1 lists the reaction energies for the epoxidations of the C (100) surface with DO, DFDO, and MTFDO. The calculated reaction profiles for the epoxidation reactions of ethylene with DO, DFDO, and MTFDO are displayed in Figure 2. It can be clearly seen that the epoxidation of the C (100) surface with DFDO is predicted to be highly exothermic by -89.4 kcal/mol, indicating that this epoxidation reaction is quite thermodynamically favorable. For the epoxidation reactions with DO and

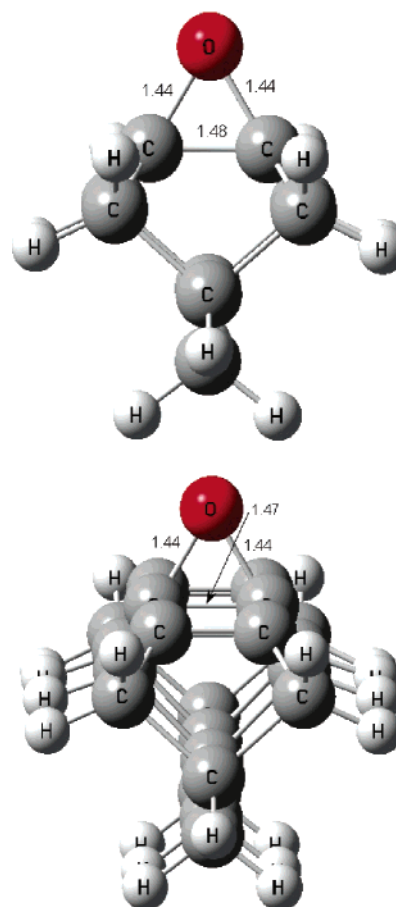


Figure 3. B3LYP/6-31G(d)-optimized geometries (units of Å for bond length) of the surface epoxide species for the epoxidation of the C (100)-2 × 1 surface with dioxiranes.

MTFDO, values of -79.4 and -80.0 kcal/mol, respectively, are predicted, which are less exothermic than that of DFDO. The results calculated using the larger cluster model $C_{21}H_{20}$ show that the size of the cluster plays a negligible effect on the reaction energetics, as has also been found in previous theoretical studies.^{6a-d,7,8} Furthermore, single-point energy calculations using the higher basis set 6-311G(2d,2p) indicate that the basis set also has a minor effect on the calculated reaction energetics. Hence, these results strongly suggest the reliability of using such a C_9H_{12} cluster model with the BL3YP/6-31G(d) method to theoretically explore the epoxidation reactions of dioxiranes with the C (100) surface.^{6a-d,7,8}

Obviously, these heterogeneous epoxidations of the C (100) surface with dioxiranes are much more exothermic than their ethylene molecular analogues. This is reasonable because of the higher reactivity of surface C=C dimers of the C (100) surface compared to ethylene, which can be attributed to the reduced overlap between the p orbitals of the surface C=C dimer.^{7,8} More interestingly, these epoxidation reactions of the C (100) surface with DO, DFDO, and MTFDO have no activation energy barrier, i.e., no transition states were located. It is the high reactivities of both the C (100) surface and the dioxiranes that lead to such epoxidation reactions proceeding without energy barrier. Note that the π -bond strength on C (100) (~ 11 – 21 kcal/mol)¹⁷ is 40 – 50 kcal/mol lower than that of a typical alkene (~ 60 kcal/mol).¹⁸ Thus, these epoxidation reactions of the reactive C (100) surface C=C dimer with dioxiranes should be expected to be facile. Similar barrierless processes were previously observed for the hydroboration of C (100) with

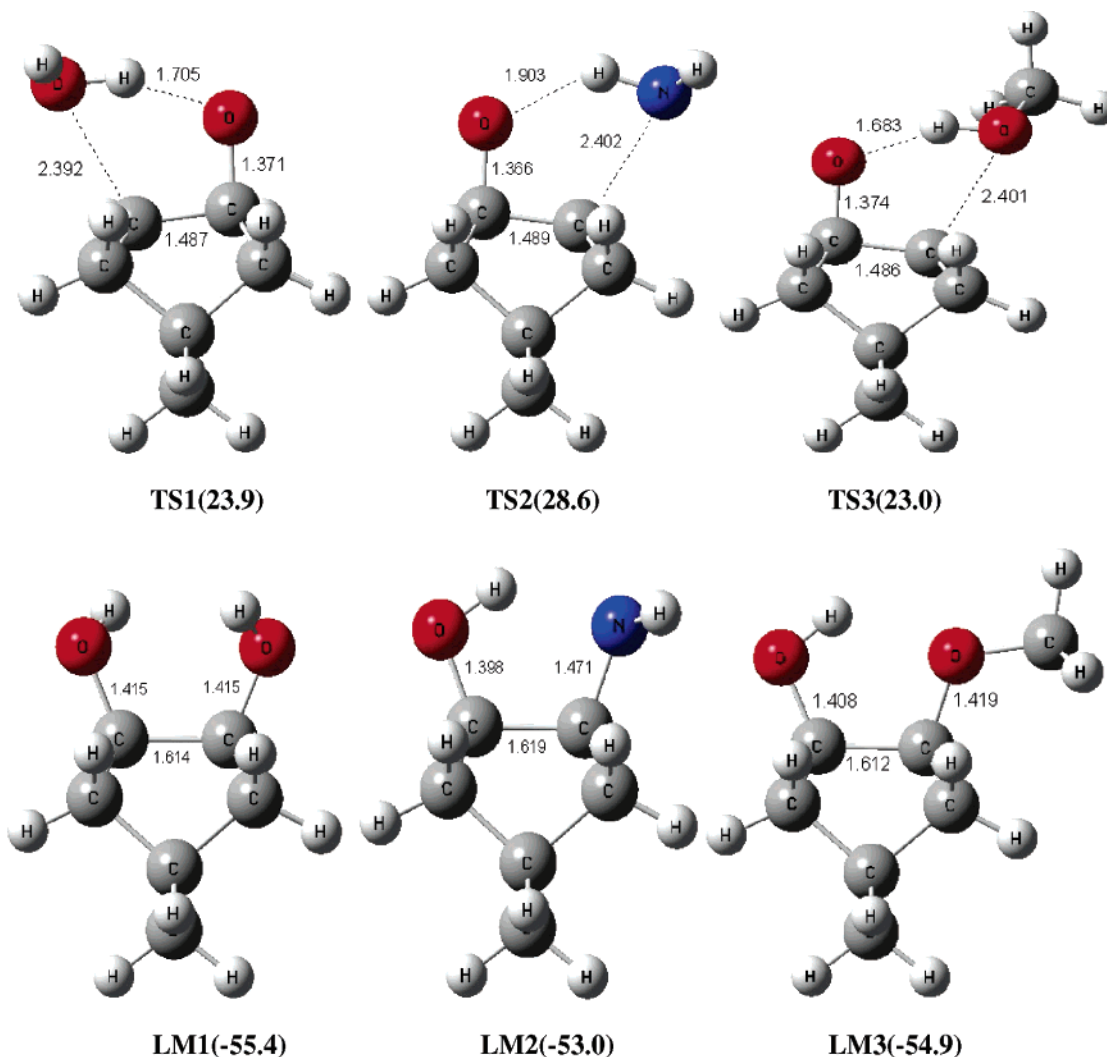


Figure 4. B3LYP/6-31G(d)-optimized geometries (units of Å for bond length) of the transition states (TS) and products (LM) for the ring-opening reactions of the as-formed epoxide surface species with H_2O , NH_3 , and CH_3OH . Energies (units in kcal/mol) relative to free reactants are given in parentheses.

borane¹⁹ as well as the additions of carbenes and nitrenes to the C (100) surface.^{7,8}

Among these three dioxiranes, the highest exothermicity suggests that DFDO seems to be the most powerful oxidant for the epoxidation of the C (100) surface. The same reactivity trend was also observed for the epoxidations of ethylene with these three dioxiranes, as shown in Table 1 and Figure 2. Theoretical investigations were also performed on the analogous epoxidation reactions of the side walls of (5,5)-SWNCTs with dioxiranes, for which activation energy barriers of 5.4, 20.6, and 22.4 kcal/mol were predicted for DFDO, DO, and MTFDO, respectively, using the ONIOM(B3LYP/6-31G*:AM1) approach.¹² For SWNCTs with larger diameters, the reactivity of the side wall decreases and the activation energy barrier increases for these heterogeneous epoxidation reactions of SWNCTs with dioxiranes.¹² As compared to their ethylene molecular analogues, these epoxidation reactions occurring on SWNCTs are much less efficient, which can be attributed to the rather high π -conjugating bonding character of the sidewalls of SWNCTs.¹² Using the semiempirical AM1 method, it was predicted that the analogous epoxidation of fullerene with MTFDO needs to surmount an activation energy barrier of 10.1 kcal/mol.^{11a} Although it is not reasonable to compare the absolute energetics for these epoxidation reactions on C (100) with those on the sidewalls of SWNCTs and fullerene because different theoretic-

cal methods were used, it can be qualitatively concluded that similar epoxidations of the C (100) surface with dioxiranes are much more favorable both thermodynamically and kinetically than those of ethylene, fullerene, and SWNCTs. That is, the reactivity of the surface $\text{C}=\text{C}$ dimer of C (100) is much higher than those of ethylene, fullerene, and SWNCTs. As such, our theoretical calculations strongly reinforce the viability of epoxidation of C (100) with dioxiranes. Meanwhile, the facility of epoxidation of diamond (100) presents a new strategy for the oxidation of the diamond (100) surface rather than using oxygen as an oxidant for which the activation energy barrier is quite high.⁵¹

Figure 3 depicts the optimized geometries of the final products, epoxide-like surface species, obtained using C_9H_{12} and $\text{C}_{21}\text{H}_{20}$ clusters. Clearly, the size of the cluster has a negligible effect on the optimized geometries, in good agreement with previous studies.^{6a-d,7,8} The epoxidation reactions of dioxiranes between two adjacent surface $\text{C}=\text{C}$ dimers was also considered using the large $\text{C}_{21}\text{H}_{20}$ cluster. However, the final optimized geometries showed that only the three-membered epoxide-like surface species can be obtained. This is reasonable given that the $\text{C}=\text{C}$ surface dimer is the most reactive site on the C (100) surface, and it also reinforces the effectiveness of using a C_9H_{12} cluster to theoretically explore the reaction of organic molecules with the C (100) surface.⁶⁻⁸ Significantly, the as-formed

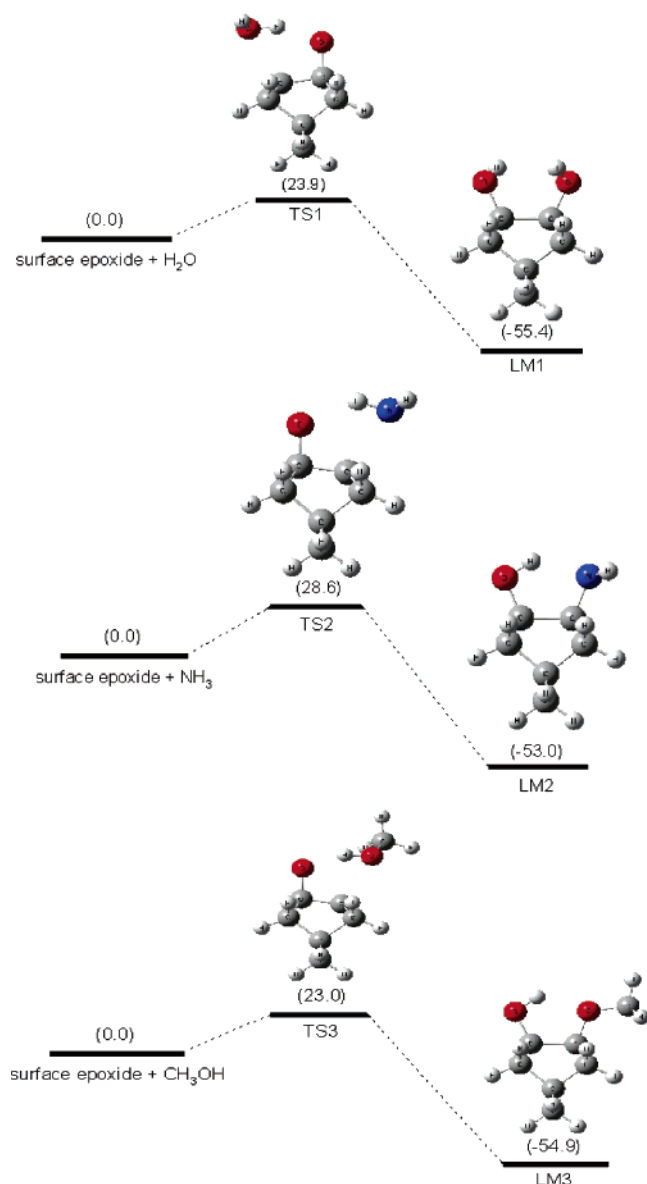


Figure 5. Theoretically calculated reaction profiles of the C (100) surface with DO, DFDO, and MTFDO at the B3LYP/6-31G(d) level of theory.

epoxide-like surface species would be subject to further chemical transformations, for example, by ring-opening reactions, given the well-known abundance of chemistry of organic epoxides.¹⁰ As is known, because of their ring strain, epoxides are very reactive to nucleophilic agents such as water, ammonia, and alcohol and can undergo ring-opening reactions.^{10c,d} Such types of possible ring-opening reactions of the as-formed epoxide surface species were thus further explored using water (H₂O), ammonia (NH₃), and methanol (CH₃OH) as model nucleophilic molecules.

As shown in Figures 4 and 5, the ring-opening reactions of the as-formed epoxide surface species with H₂O, NH₃, and CH₃OH are predicted to be quite exothermic by -55.4, -53.0, and -54.9 kcal/mol, respectively. At the same time, the calculations searching for transition states illustrate that these ring-opening reactions need to surmount activation energy barriers of 23.9, 28.6, and 23.0 kcal/mol for H₂O, NH₃, and CH₃OH, respectively. This suggests that the ring-opening reactions of the as-formed epoxide surface species could possibly occur at elevated temperatures. Thus, the surface epoxide species could be used as starting points for anchoring a wide variety of func-

tional groups, possibly imparting other new functionalities to the diamond surface. In this regard, the well-established chemistry of organic epoxides can be adopted to functionalize the diamond surface for specific applications.¹⁰ As such, analogous epoxidation reactions of dioxiranes with ethylene, C (100), SWNCTs, and fullerene have been reported, strongly suggesting that quite intriguing chemistry might lie in the materials, featuring analogous bonding motifs, and that there is an intrinsic relationship between structure and reactivity.^{11,12}

Disilenes, digermenes, silenes, germenes, Si (100), and Ge (100) all have bonding motifs similar to those of ethylene, diamond (100), fullerene, and SWNCTs.^{20,21} In other words, the bonding motifs of all of these substances can typically be depicted as a strong σ bond and a weak π bond, implying that similar chemistry might exist among them. Thus, a question naturally arises as to the nature of the reaction profiles of similar epoxidations of these substances with dioxiranes and subsequent ring-opening reactions. To address this issue and understand the underlying reaction mechanisms at the molecular level would certainly be interesting not only from a fundamental standpoint but for potential technological applications. Theoretical explorations in this regard would add much to the richness of chemistry of solid surfaces and organic/inorganic chemistry. Further comprehensive theoretical work along this line is in progress.

In addition, it should be mentioned that our main purpose herein is to qualitatively predict the possibility of the epoxidation of diamond (100) by dioxiranes and further ring-opening reactions with nucleophiles, based on the calculated activation energy barriers and reaction energies. Reaction rates and reaction free energies are not addressed in our calculations. However, note that a recent study has proposed a simple statistical mechanics model that allows the use of electronic structure calculations to determine adsorption reaction free energies on solid surfaces.²² A similar simple model to predict reaction kinetics on solid surfaces is urgently needed, because such types of models can help in the effective prediction of other important reaction parameters, namely, reaction free energies and reaction rates, as is generally done in the case of gas-phase and solution-phase reactions.

4. Concluding Remarks

In summary, we have predicted the viability of the epoxidation of the diamond (100) surface with organic dioxiranes. Moreover, the surface epoxide species can be used as precursors for further chemical functionalizations of the diamond surface, for example, by ring-opening with nucleophiles. Thus, the well-established chemistry of organic epoxides could be flexibly employed to functionalize the diamond surface by introducing other new functional groups. Our results provide another example that the diamond (100) surface can be functionalized by synthetic organic chemistry and, more importantly, offer a new route to functionalize the diamond surface, which is potentially useful for constructing new diamond-based hybrid materials for specific uses in many fields. In addition, the ease of the epoxidation of diamond (100) by dioxiranes also offers a new strategy for the oxidation of diamond surfaces rather than using oxygen as an oxidant. In the latter case, the activation energy barrier is quite high.⁵¹ At the same time, it should be mentioned that other oxidants, such as peroxy acids and hypofluorous acid, can also epoxidize alkenes^{9c,23} and fullerenes.²⁴ We believe that the epoxidation of diamond (100) with these oxidants should also be viable.

Meanwhile, our theoretical predictions strongly advance the concept of using organic reactions to modify solid surfaces and

that quite intriguing chemistry can lie in materials featuring analogous bonding motifs. In a broad perspective, the similarity of the bonding motifs of disilenes, digermenes, silenes, germenenes, Si (100), and Ge (100) to those of ethylene, diamond (100), fullerene, and SWNTs inspires us to further theoretically explore the profiles of epoxidation of these substances with dioxiranes and subsequent ring-opening reactions of the as-formed surface epoxides. By comparison, the analogies and differences among them can be found, thus adding much to the richness and diversity of solid surface chemistry and organosilicon/organogermanium chemistry. We look forward to experimental realization of the reactions predicted herein, as well as the potential applications of the as-functionalized diamond surfaces.

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