Epoxide reduction with hydrazine on graphene: A first principles study

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Mechanisms for epoxide reduction with hydrazine on a single-layer graphene sheet are examined using quantum mechanical calculations within the framework of gradient-corrected spin-polarized density-functional theory. We find that the reduction reaction is mainly governed by epoxide ring opening which is initiated by H transfer from hydrazine or its derivatives. In addition, our calculations suggest that the epoxide reduction by hydrazine may predominantly follow a direct Eley–Rideal mechanism rather than a Langmuir–Hinshelwood mechanism. We also discuss the generation of various hydrazine derivatives during the reduction of graphene oxide with hydrazine and their potential contribution to lowering the barrier height of epoxide ring opening. © 2009 American Institute of Physics. [DOI: 10.1063/1.3197007]

I. INTRODUCTION

Since its discovery a few years ago, there has been much excitement about graphene-based materials. Graphene refers to a flat monolayer of carbon atoms packed into a two-dimensional (2D) honeycomb lattice. The 2D crystalline structure opens up a new class of materials with novel electronic, optical, and mechanical properties.¹⁻⁷ While offering great promise for many exciting new applications, graphene-based technology currently suffers from the lack of method for high-yield production of graphene. One promising approach that is currently being explored extensively is chemically reduced to obtain graphene as individual sheets. The exfoliated GO can be hydrophilic, thereby stabilizing them to be easily exfoliated in aqueous media. The exfoliated GO can be chemically reduced to obtain graphene as individual sheets. An effective reduction method is that of placing a graphite oxide paper into a solution of pure hydrazine.¹¹ The hydrazine reduction in GO results in significant restoration of epoxidelike structure and often leaves a number of defects.8–11 Despite its importance, only a very limited effort¹⁰ has been undertaken to understand the mechanism of the hydrazine reduction reaction. In this paper, we present viable pathways for removal of an isolated epoxide group from the graphene surface with hydrazine species based on spin-polarized density-functional theory (DFT) calculations.

II. COMPUTATIONAL METHODS

All atomic structures and energies reported herein were calculated within the GGA (PW91) (Ref. 12) to spin-polarized DFT using the well-established Vienna ab initio simulation package (VASP).¹³ A plane-wave basis set for valence electron states and Vanderbilt ultrasoft pseudopotentials for core-electron interactions were employed. A plane-wave cutoff energy of 300 eV was used for ab initio molecular dynamics (AIMD) simulations and 400 eV for static structure energy calculations. The Brillouin zone integration was performed using a (4×4×1) Monkhorst–Pack (MP) mesh of k points for static calculations and a (2×2×1) MP mesh for AIMD simulations. In the calculations, periodic boundary conditions with a 32-atom model graphene sheet were employed in all three directions with a vacuum gap of 12 Å in the z direction to separate two distinct surfaces. We used the generalized gradient approximation (GGA)-optimized lattice constant, a=2.467 Å, which is slightly larger than the experimental value, 2.461 Å. All atoms were relaxed using the conjugate gradient method until residual forces on constituent atoms became smaller than 1 × 10⁻² eV/Å. We carefully checked the convergence of atomic configurations and relative energies with respect to plane-wave energy cutoff, supercell size, and k-point mesh size, confirming that the relative energy variations are in the order of 0.1 eV with unnoticeable changes in the atomic structure. Indeed, the chosen parameters have been found to yield well-converged results for the structure and chemistry of graphite materials.¹⁴⁻¹⁷ We used the nudged elastic band method with 16 intermediate images to determine reaction pathways and barriers, together with the dimer method for the sake of confirmation when necessary.

III. RESULTS AND DISCUSSION

A. O and OH adsorption structure

Earlier theoretical studies¹⁴⁻¹⁷ showed that the site above the middle of a C–C bond is most favorable for atomic oxygen adsorption on the basal plane of graphite, resulting in an epoxidelike structure [left panels in Fig. 1(a)]. Our DFT GGA calculation gives the O binding energy of E_b(O)
phase $O_2$ in the triplet state, respectively. The $O$–$C$–$C$ bond
energies of graphene with an epoxide group, graphene, and gas-
phase $O_2$, are estimated to be 60.3°, 1.50 Å, and 1.48 Å in ang-
stroms and bond angles (in degree) are also indicated.

\[ E_b(O) = -E_{O/graphene} + E_{graphene} + 1/2E_{O_2}, \]

where $E_{O/graphene}$, $E_{graphene}$, and $E_{O_2}$ represent the total ener-
gies of graphene with an epoxide group, graphene, and gas-
phase $O_2$ in the triplet state, respectively. The $O$–$C$–$C$ bond
angles and $C$–$O$ and $C$–$C$ bond lengths of the equilateral
triangle structure are estimated to be 60.3°, 1.50 Å, and 1.48 Å,
respectively.

As shown in Fig. 1(a) (right panels), we also considered
$O$ adsorption on top of a $C$ atom, but the on-top structure
easily converts to the epoxide structure with an exothermic-
ity of 13.4 kcal/mol. On the other hand, as illustrated in Fig.
1(b) an $OH$ radical favors the on-top site (directly above a $C$
atom) (right panels) on the defect-free graphene surface,
while the $C$–$C$ bridge site is very unfavorable for $OH$
adsorption (left panels). The predicted $OH$ binding energy at the
top site is 15.4 kcal/mol ($=E_{OH/graphite} + E_{graphite} + E_{OH}$
where $E_{OH}$ refers to the total energy of gas-phase $OH$), close to
other DFT-GGA values.\(^{15}\) The result demonstrates that hy-
drogenation of the epoxide $O$ atom will lead to opening of the
epoxy ring.

**B. Epoxide reduction by $N_2H_4$**

A $N_2H_4$ molecule consists of two pyramidal $H_2N$ sub-
units which are free to rotate with respect to each other along
the $N$–$N$ single bond. The preferred configuration of $N_2H_4$
is gauche where the electron lone pairs remain approximately
perpendicular. Our DFT calculations show that the $N_2H_4$
molecule can be bound to an epoxide due to electrostatic
attraction between a positively charged $H$ in $N_2H_4$ and the
negatively charged $O$ in epoxide. The predicted energy gain
is about 4.5 kcal/mol, which is greater than 1.9 kcal/mol
estimated for the typical $N$–$H$–$O$ hydrogen bond energy. The
binding strength of $N_2H_4$ to the O/graphene surface is not
substantial but greater than the average thermal energy at
room temperature ($=0.6$ kcal/mol).

Figure 2 shows a pathway for epoxide ring opening via
$H$ abstraction from $N_2H_4$, together with an energy variation
along the reaction coordinate. The ring-opening reaction is
predicted to be nearly thermoneutral while requiring over-
coming a barrier of 10.2 kcal/mol which is lower than 13.4
kcal/mol in the absence of $N_2H_4$ [Fig. 1(a)]. As illustrated in
Fig. 1(b), the resulting $OH$ group favorably resides atop a $C$
atom. The results evidently demonstrate that the ring opening
of epoxides can be facilitated by hydrazine treatment.

After the first $H$ abstraction, as shown in Fig. 3, the
$NHNH_2$ moiety tends to stay around the $OH$ group bound to
the graphene surface (indicated as HO-gr hereafter) due to
the electrostatic interaction between the positively charged $H$
(in HO-gr) and the negatively charged $N$ (in $NHNH_2$) and/or

**FIG. 1.** Top and side views of the optimized adsorption structures of (a)
atomic oxygen and (b) hydroxyl radical at the $C$–$C$ bridge site (left) and the
$C$ atop site (right). The gray (gray), red (black), and white (white) balls
represent $C$, $O$, and $H$ atoms, respectively. Selected bond lengths
and bond angles are given in angstroms [hydrogen bonds are indicated by a dashed line (---)].

**FIG. 2.** Optimized configurations for the initial (IS), transition (TS), and
final (FS) states of epoxide ring opening via $H$ abstraction from hydrazine ($N_2H_4$) together with corresponding activation energy and exothermicity (in
cal/mol). For each state, both top and side views are presented. The gray
(gray), red (black), cyan (gray in hydrazine), and white (white) balls
represent $C$, $O$, $N$, and $H$ atoms, respectively. The bond lengths indicated are
given in angstroms [hydrogen bonds are indicated by a dashed line (---)].

**FIG. 3.** Snapshots from AIMD for $OH$ hydrogenation via $H$ abstraction from
$NHNH_2$. The gray (gray), red (black), cyan (gray in $NHNH_2$), and white
(white) balls represent $C$, $O$, $N$, and $H$ atoms, respectively.
leading to coadsorption of OH and NHNH2 at two adjacent sites. The corresponding activation energy and exothermicity due primarily to alternation of three pairwise electrostatic interactions such as O–H$^\delta_-$−N$^{\delta_-}$−HNH2, H−O$^{\delta_-}$−H$^{\delta_-}$−NNH2, and H−O$^{\delta_-}$−H$^{\delta_-}$−NNH2. However, unlike the flying case, no additional H abstraction from the anchored NHNH2 occurs within a few picoseconds of AIMD simulation time at 500 K.

As presented in Fig. 5, we therefore used a transition search method to calculate the OH hydrogenation reaction, i.e., HO-gr+NH2NH-gr→H2O(g)+NH2N-gr. The reaction is predicted to occur by crossing a barrier of 6.7 kcal/mol with an exothermicity of 23.0 kcal/mol, while the remaining N2H2 molecule subsequently desorbs with practically no barrier. Note that the OH hydrogenation barrier is comparable to 6.2 kcal/mol for NHNH2 desorption from the graphene surface. If so, considering entropy effects the NHNH2 desorption can be kinetically more facile than the OH hydrogenation. Indeed, a series of AIMD simulations at 500 K with varying initial HO-gr and NH2NH-gr configurations demonstrates the occurrence of NHNH2 desorption (while NHNH2 interacts electrostatically with HO-gr) but not OH hydrogenation. Upon desorption, NH2NH easily donates a H atom to HO-gr, leading to H2O and N2H2 formation as also seen earlier in the direct ER process. The results suggest that the hydrazine reduction of epoxides may predominantly follow the direct ER mechanism rather than the Langmuir–Hinshelwood (LH) mechanism.
and side views are presented. The gray together with the corresponding activation energy and exothermicity. In addition, the barrier height of 3.6 kcal/mol is noticeably lower than 10.2 energy variation along the reaction coordinate. The predicted reduction of HO-gr with N2H4, which turns out to have a small barrier (≈3.5 kcal/mol). Our calculations demonstrate that epoxide reduction in graphene is mainly determined by ring opening that is facilitated by the presence of hydrazine and its derivatives as a source of hydrogen.

IV. SUMMARY

Atomic mechanisms for epoxide reduction with hydrazine on graphene are presented based on gradient-corrected spin-polarized DFT calculations. For this study, an epoxide group is placed on a graphene sheet which is modeled using a 32-atom periodic supercell. Our calculations clearly demonstrate that the epoxide is reduced to form H2O by two successive hydrogenation reactions which involve H abstraction from hydrazine and/or its derivatives. We examined two possible mechanisms, direct ER and LH. We find that both mechanisms are possible with comparable activation barriers (of about 6 kcal/mol), but the ER route is likely to be more kinetically facile. Our study also suggests possible creation of reactive hydrazine derivatives such as NNNH2 during reduction of GO sheets by hydrazine, while they can contribute to facilitating epoxide reduction. Here we should admit that the reaction of hydrazine species with epoxides in the solution phase (such as pure hydrazine and hydrazine hydrate) may involve other important elementary steps that are not shown in the gas-phase reaction reported herein, which warrants further investigation. Nonetheless, the improved understanding of the hydrazine-epoxide interaction will assist in better understanding atomistic mechanisms underlying the hydrazine reduction of GO sheets.

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Finally, we looked at the possibility that hydrazine derivatives such as NNNH2 will contribute to the epoxide reduction. Figure 6 shows a viable pathway that we identified for epoxy ring opening with NNNH2, together with an energy variation along the reaction coordinate. The predicted barrier height of 3.6 kcal/mol is noticeably lower than 10.2 kcal/mol as estimated for the NNNH4 case. In addition, the ring-opening reaction with NNNH2 is predicted to be exothermic by 12.3 kcal/mol, whereas the exothermicity of the NNNH4 case is only 0.3 kcal/mol (albeit practically thermoneutral, see Fig. 2). The relatively facile H abstraction is not surprising considering that NNNH2 is far less stable than NNNH4 in nature. As illustrated in Fig. 7, we also calculated the reduction of HO-gr with N2H4, which turns out to have a small barrier (≈3.5 kcal/mol). Our calculations demonstrate that epoxide reduction in graphene is mainly determined by ring opening that is facilitated by the presence of hydrazine and its derivatives as a source of hydrogen.

FIG. 6. Optimized configurations for the initial (IS), transition (TS), and final (FS) states of epoxide ring opening via H abstraction from NNNH2, together with the corresponding activation energy and exothermicity. In addition, the barrier height of 3.6 kcal/mol is noticeably lower than 10.2 energy variation along the reaction coordinate. The predicted reduction of HO-gr with N2H4, which turns out to have a small barrier (≈3.5 kcal/mol). Our calculations demonstrate that epoxide reduction in graphene is mainly determined by ring opening that is facilitated by the presence of hydrazine and its derivatives as a source of hydrogen.

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FIG. 7. Optimized configurations for the initial (IS), transition (TS), and final (FS) states of OH hydrogenation via H abstraction from NNNH2. The reaction is predicted to occur with a small barrier (≈3.5 kcal/mol) while releasing a large exothermicity (≈27.4 kcal/mol). For each state, both top and side views are presented. The gray (gray), red (black), cyan (gray), and white (white) balls represent C, O, N, and H atoms, respectively. The bond lengths indicated are given in angstroms [hydrogen bonds are indicated by a dashed line (---)].