

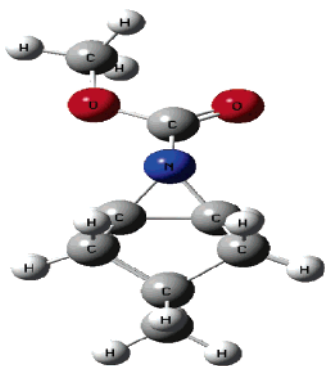
Functionalization of Diamond (100) by Organic Cycloaddition Reactions of Nitrenes: A Theoretical Prediction

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

School of Chemistry, Main Building, Cardiff University, Cardiff, CF10 3AT, U.K., and Department of Chemistry, Fuzhou University, Fuzhou, 350002, China

XuY7@cf.ac.uk

Received July 4, 2005



We predict the viability of organic cycloadditions of nitrenes onto the diamond (100) surface. This new type of surface reaction can be employed to functionalize diamond surface at low temperature, which might introduce new functionalities to the diamond surface for novel applications in a diversity of fields.

Owing to its fascinating and unique mechanical, electrical, and optical combination of material properties, the diamond has been attracting considerable interest and attention as a promising candidate for a wide range of applications.^{1–4} The chemical functionalization of the diamond surface can be potentially useful to tailor its properties for specific applications.⁵ Hence, it is of paramount interest both fundamentally and technologically to explore the chemistry of the diamond surface and to seek specific methods of making controlled chemical functionalizations of diamond surfaces. Toward this end, we report a theoretical study of the additions of nitrenes onto the C(100)-2 × 1 surface. Our prediction suggests that this new type of surface reactions can be employed to functionalize the diamond surface at low temperature.

Indeed, recently, great effort has been devoted to using organic reactions to modify the C(100)-2 × 1 surface.⁶

[†] Cardiff University.

[‡] Fuzhou University.

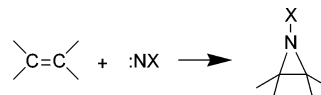
(1) Ashfold, M. N. R.; May, P. W.; Rego, C. A.; Everitt, N. M. *Chem. Soc. Rev.* **1994**, *23*, 21.

(2) *The Properties of Natural and Synthetic Diamond*; Field, J. E. Ed.; Academic Press: London, 1992.

(3) Hossain, Z.; Kubo, T.; Aruga, T.; Takag, N.; Tsuno, T.; Fujimori, N.; Nishijima, M. *Jpn. J. Appl. Phys.* **1999**, *38*, 6659.

(4) Wei, J.; Yates, J. T., Jr. *Crit. Rev. Surf. Chem.* **1995**, *5*, 1.

SCHEME 1. Addition of Nitrenes to Alkenes



This interest largely arises from the hope that the wide range of functionalities of organic molecules can be potentially added to the diamond surface. For example, it was theoretically predicted that 1,3-dipolar cycloadditions of a series of 1,3-dipolar molecules onto the C(100) surface are much more favorable over their molecular analogues both thermodynamically and kinetically.^{6a,b} Similarly, another class of Diels–Alder reactions has been intensively studied with regard to the surface C=C dimer of the C(100) surface.^{6c,d} More fascinating is the experimental work done at room temperature, reported by Wang et al., that 1,3-butadiene can react with the C(100) surface to form a Diels–Alder adduct at room temperature.^{6e} Very recently, we predicted that the C(100) surface can be functionalized by the well-known addition reactions of carbenes to olefins in organic chemistry.⁷ These findings are rather encouraging and significant because they strongly demonstrate the feasibility of functionalizing diamond surfaces by means of synthetic organic chemistry, which may consequently lead to a breakthrough in the fabrication of diamond films at low temperature.

It is well-known that, in organic chemistry, nitrenes are a fascinating class of highly reactive species.⁸ The representative organic reaction of nitrenes is their addition to olefins (as shown in Scheme 1), and the so-formed aziridine is very versatile for further chemical transformations.⁸

Like singlet carbenes, singlet nitrenes are highly electron-deficient,^{7,8} whereas the surface C=C dimer of C(100) is highly nucleophilic.⁷ Therefore, several representative singlet nitrenes can be used as excellent model molecules to assess whether the C(100) surface can be functionalized by the addition reaction of nitrenes toward

(5) For examples, see: (a) Miller, J. B.; Brown, D. W. *Langmuir* **1996**, *12*, 5809. (b) Strother, T.; Knickerbocker, T.; Russell, J. N.; Butler, J. E.; Smith, L. M.; Hamers, R. T. *Langmuir* **2002**, *18*, 968. (c) Ida, S.; Tsubota, T.; Tanii, S.; Nagata, M.; Matsumoto, Y. *Langmuir* **2003**, *19*, 9693. (d) Potochnik, S. J.; Pehrsson, P. E.; Hsu, D. S.; Calvert, J. M. *Langmuir* **1995**, *11*, 1841. (e) Mackey, B. L.; Russell, J. N., Jr.; Crowell, J. E.; Butler, J. E. *Phys. Rev. B* **1995**, *52*, 17009. (f) Pickett, W. E. *Phys. Rev. Lett.* **1994**, *73*, 1664. (g) Smentkowski, V. S.; Yates, J. T., Jr. *Science* **1996**, *271*, 193. (h) Ida, S.; Tsubota, T.; Hirabayashi, O.; Nagata, M.; Matsumoto, Y.; Fujishima, A. *Diamond Relat. Mater.* **2003**, *12*, 601. (i) Goeting, C. H.; Marken, F.; Gutierrez-Sosa, A.; Compton, R. G.; Foord, J. S. *Diamond Relat. Mater.* **2002**, *9*, 390. (j) Liu, Y.; Gu, Z.; Margrave, J. L.; Khabashesku, V. N. *Chem. Mater.* **2004**, *16*, 3924. (k) Tsubota, T.; Tanii, S.; Ida, S.; Nagata, M.; Matsumoto, Y. *Diamond Relat. Mater.* **2004**, *13*, 1093.

(6) (a) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *J. Org. Chem.* **2002**, *67*, 515. (b) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *J. Phys. Chem. B* **2002**, *106*, 5972. (c) Okamoto, Y. *J. Phys. Chem. B* **2001**, *105*, 1813. (d) Fitzgerald, D. R.; Doren, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 12334. (e) Wang, G. T.; Bent, S. F.; Russell, J. N., Jr.; Butler, J. E.; D'Evelyn, M. P. *J. Am. Chem. Soc.* **2000**, *122*, 744.

(7) Xu, Y. J.; Zhang, Y. F.; Li, J. Q. *J. Org. Chem.* **2005**, *70*, 6089.

(8) (a) *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: New York, 1974. (b) *Nitrenes*; Lwowski, W., Ed.; Wiley-Interscience: New York, 1970. (c) Wentrup, C. *Reactive Intermediates*; Wiley: New York, 1984. (d) *Reactive Intermediate Chemistry*; Moss, R. A.; Platz, M. S.; Jones, M., Jr., Eds.; Wiley: New York, 2003.

the surface C=C double bond. In this note, parent nitrene (NH), aminonitrene (NNH₂), and oxycarbonylnitrene (NCOOCH₃) were selected as testing model molecules. On the other hand, it is worthwhile to note that analogous nitrene addition reactions have successfully been reported regarding the functionalization of the single wall carbon nanotube (SWCNT) and fullerene.⁹ Strongly inspired by these pioneering chemical precedents, we naturally infer that similar cycloaddition reactions should take place on the C(100)-2 × 1 surface. Here, we report the computational description of the reactions of nitrenes with the C(100) surface.

A C₉H₁₂ cluster model was employed to represent a dimer site on the C(100) surface. Larger cluster model C₂₁H₂₀ was used to confirm the results obtained from a C₉H₁₂ cluster. This surface model was successfully used in our recent theoretical prediction of the additions of parent carbene, silylene, and germylene onto the C(100)-2 × 1 surface.⁷ Meanwhile, this surface model has been used in the theoretical studies of the 1,3-polar cycloadditions and the Diels–Alder reactions on the C(100)-2 × 1 surface.^{6a–d} Furthermore, cluster models present the advantage in terms of a compromise of accuracy and computational cost if clusters are properly selected.^{7,10} The hybrid density functional B3LYP method¹¹ and the standard 6-31G(d) basis sets were employed. Recent studies have consistently reinforced the reliability of using this theoretical method to study surface reactions on the C(100)-2 × 1 surface.^{6a–d,7} Geometry optimizations with no constrained degrees of freedom were carried out using analytical gradients and the Berny algorithm. Reported energies were zero-point vibration energy (ZPVE) corrected. Single-point calculations were done, using the 6-311G(2d,2p), to investigate the basis set effect on the reaction energetics. In addition, these surface reactions were compared to those of gas-phase ethylene molecular analogue and available data for fullerene and SWCNT in the literature. All the calculations were performed with the Gaussian 98 program.¹²

Table 1 lists the reaction energies for the additions of parent nitrene, aminonitrene, and oxycarbonylnitrene onto the C(100) surface, respectively. The predicted reaction energy is –144.6 kcal/mol for the addition of the prototype nitrene, NH, onto the C(100) surface, indicating that this surface reaction is quite highly exothermic. This is similar to that of singlet carbene (CH₂) addition to the surface dimer of C(100) surface, for which an exothermicity of –134.0 kcal/mol is predicted at the same theoretical level.⁷ What is more, the addition of NH onto the surface C=C dimer has no activation energy barrier

TABLE 1. Calculated Activation Energies (ΔE_a , in kcal/mol) and Reaction Energies (ΔE_r , in kcal/mol) for the Addition Reactions of Nitrene, Aminonitrene, and Oxycarbonylnitrene onto the C(100)-2 × 1 Surface

system	method ^a	ΔE_a	ΔE_r
NH + C ₉ H ₁₂	B3LYP/6-31G(d)	–	–144.6
	B3LYP/6-311G(2d,2p)	–	–142.3
NNH ₂ + C ₉ H ₁₂	B3LYP/6-31G(d)	–	–52.7
	B3LYP/6-311G(2d,2p)	–	–51.8
NCOOCH ₃ + C ₉ H ₁₂	B3LYP/6-31G(d)	–	–103.9
	B3LYP/6-311G(2d,2p)	–	–101.6
NH + ethylene	B3LYP/6-31G(d)	–	–102.9
NNH ₂ + ethylene	B3LYP/6-31G(d)	7.7	–21.3
NCOOCH ₃ + ethylene	B3LYP/6-31G(d)	3.5	–77.8

^a The use of larger cluster C₂₁H₂₀ has a negligible effect on the calculations of reaction energies and geometries of products (see Supporting Information).

that is exactly the same as that of CH₂ addition to the C(100) surface and ethylene, respectively.^{7,13} *It is the high reactivity of both the C(100) surface and parent nitrene- (or carbene) that leads to the addition reaction proceeding without energy barrier.* In fact, the addition of NH to ethylene was also predicted without energy barrier, the same as the addition of CH₂ to ethylene.¹³ A similar barrierless process was observed for the hydroboration of C(100) with borane, a strong Lewis acid.¹⁴

With regard to the addition of oxycarbonylnitrene onto the C(100) surface, our calculations predicted an exothermicity of –103.9 kcal/mol, suggesting that this surface addition reaction is still very thermodynamically favorable. Very interestingly, similar to that of parent nitrene, this surface reaction is barrierless, that is, no transition states are located. This strongly demonstrates the viability of the addition of nitrenes onto the reactive surface C=C dimer. Previously, analogous cycloaddition of singlet oxycarbonylnitrene onto fullerene was reported for which an activation energy of only 3.6 kcal/mol was predicted using the ONIOM(B3LYP/6-31G*:AM1) approach.¹⁵ Whereas, for the addition of singlet oxycarbonylnitrene onto the sidewall of (5,5)-SWCNT, a small activation energy barrier of 7.2 kcal/mol was predicted using the ONIOM(B3LYP/6-31G*:AM1) level of theory.¹⁶ Our results clearly illustrate that the addition of singlet oxycarbonylnitrene onto the surface C=C dimer of the C(100) surface is much more favorable both thermodynamically and kinetically than that of the SWCNT and fullerene. These results also suggest the much higher reactivity of the surface C=C dimer of C(100) than that of fullerene

(9) For examples, see: (a) Holzinger, M.; Abraham, J.; Whelan, P.; Graupner, R.; Ley, L.; Hennrich, F.; Kappes, M.; Hirsch, A. *J. Am. Chem. Soc.* **2003**, *125*, 8566. (b) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002. (c) Hirsch, A. *The Chemistry of Fullerenes*; Thieme: Stuttgart, Germany, 1994. (d) Diederich, F.; Issacs, L.; Philip, D. *Chem. Soc. Rev.* **1994**, 243. (e) Smith, A. B., III; Tokuyama, H. *Tetrahedron* **1996**, *52*, 5257.

(10) (a) Xu, Y. J.; Li, J. Q.; *Chem. Phys. Lett.* **2005**, *406*, 249. (b) Xu, Y. J.; Li, J. Q.; Zhang, Y. F.; Chen, W. K. *J. Chem. Phys.* **2004**, *120*, 8753. (c) Xu, Y. J.; Li, J. Q. *Chem. Phys. Lett.* **2004**, *400*, 406. (d) Xu, X.; Nakatsui, H.; Lu, X.; Ehara, M.; Cai, Y.; Wang, N.; Zhang, Q. *Theor. Chem. Acc.* **1999**, *172*, 170. (e) Xu, Y. J.; Li, J. Q.; Zhang, Y. F.; Chen, W. K. *Surf. Sci.* **2003**, *525*, 13. (f) Fu, G.; Xu, X.; Lu, X.; Wang, H. *J. Am. Chem. Soc.* **2005**, *127*, 3989.

(11) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. A* **1988**, *37*, 785.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654.

(14) Long, L.; Lu, X.; Tian, F.; Zhang, Q. *J. Org. Chem.* **2003**, *68*, 4495.

(15) Cases, M.; Duran, M.; Solà, M. *J. Mol. Model.* **2000**, *6*, 205.

(16) Lu, X.; Tian, F.; Zhang, Q. *J. Phys. Chem. B* **2003**, *107*, 8388.

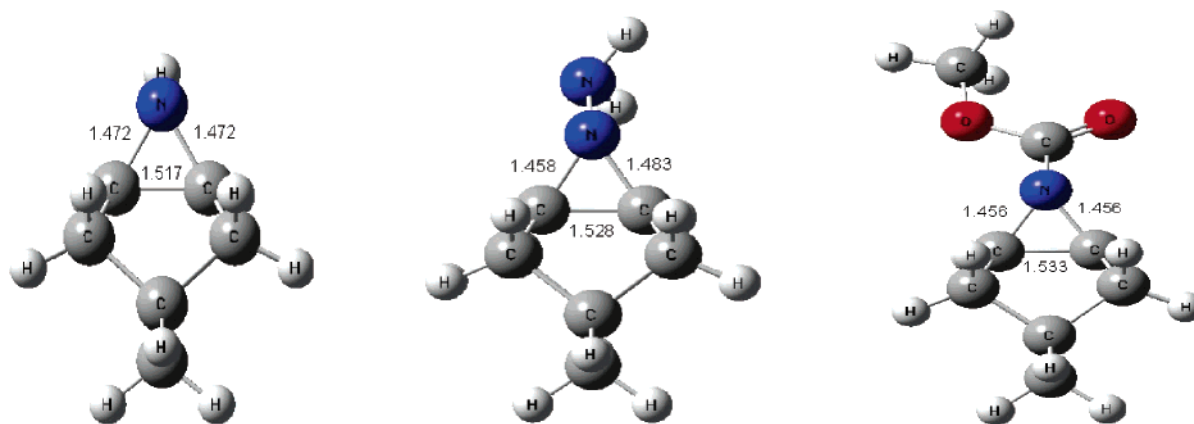


FIGURE 1. B3LYP/6-31G(d) optimized geometries (units in angstroms for bond length) of the additions of nitrene, aminonitrene, and oxycarbonylnitrene onto the C(100)-2 × 1 surface.

and SWCNT which can be ascribed to the rather high π -conjugation bonding character.

For the addition of aminonitrene onto the C(100) surface, it was predicted to be exothermic by -52.7 kcal/mol, which is much lower than that of the additions of NH and oxycarbonylnitrene onto the C(100) surface. This indicates that the different substituents should have an important effect on the addition profile of nitrenes onto the C(100) surface. However, detailed calculations of searching transition state still show that this surface addition reaction is barrierless. Hence, our calculations strongly reinforce the viability of using nitrene addition to functionalize the C(100) surface. More significantly, our results strongly suggest that this kind of organic addition reactions can be used as a new type of surface organic reactions to functionalize the diamond surface. In practice, nitrenes can be produced by the process of photolysis and thermolysis at moderate temperature (for example, oxycarbonylnitrenes can be generated by thermal elimination of N_2 from organic azides)⁸ and therefore introduced onto the C(100) surface.

On the other hand, it can be clearly seen that the additions of these three selected nitrenes onto the C(100) surface are much more favorable both thermodynamically and kinetically than their ethylene molecular analogues. This is faithfully consistent with the much higher reactivity of the surface C=C dimer than ethylene, which can be ascribed to the reduced overlap between the p orbitals of the surface C=C dimer of the C(100) surface.^{6a-d,7}

Figure 1 depicts the optimized geometries of the products. It is noteworthy that the as-formed products have an aziridine-like (three-membered) structure that would be subject to ring-opening reactions accompanied with the attachment of other organic functional groups,¹⁷ hence possibly imparting other new functionalities to the diamond surface. As is well-known, aziridine can be used as a convenient springboard to other functionality by ring-opening with nucleophiles, elimination, or rearrangement.¹⁷ Thus, in this regard, the well-established synthetic methods for aziridine ring-opening chemistry can be further applied to modify the diamond surface.¹⁷

(17) For reviews about aziridine chemistry, see: (a) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599. (b) Sweeney, J. B. *Chem. Soc. Rev.* **2002**, *31*, 247. (c) Muller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905.

In summary, we predicted the viability of using nitrene addition reactions to functionalize the diamond (100) surface. The high reactivity of both the diamond (100) surface and nitrenes leads to the conclusion that the predicted organic addition of nitrenes onto the C(100) surface is rather facile, similar to that of carbenes.⁷ More significantly, the abundance of well-established aziridine ring-opening chemistry would provide high flexibility of functionalizing the as-formed aziridine-like surface species. This will contribute to develop a new organic-inorganic functional material, which incorporates the physical functions of diamond and the chemical functions of organic functional groups, thus possibly leading to novel applications of diamond films at low temperature. Furthermore, our results strongly advance the concept of using organic reactions to modify the solid surface.^{7,18,19} More detailed work is in progress to investigate in what manner the reaction profile (including reaction energetics, reaction paths, and the effect of spin multiplicity) would change for the additions of various substituted nitrenes onto the C(100)-2 × 1 surface.

In a broader perspective, this kind of surface organic reactions can also be extended to modify the Si(100) and Ge(100) surfaces featuring the bonding motif in the surface dimer analogous to that of the C(100) surface.^{18,19} We look forward to experimental realization of the reaction predicted herein and the potential applications of as-functionalized diamond surfaces.

Acknowledgment. The support of the Natural Science Foundation of China is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates and number of imaginary frequencies (NIMAG) of the optimized geometries, and the calculated reaction energies and geometries using larger cluster $C_{21}H_{20}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO051383S

(18) (a) Buriak, J. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 532. (b) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. M.; Russell, J. N., Jr. *Acc. Chem. Res.* **2000**, *33*, 617.

(19) (a) Filler, M. A.; Bent, S. F. *Prog. Surf. Sci.* **2003**, *73*, 1. (b) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271. (c) Lu, X.; Lin, M. C. *Int. Rev. Phys. Chem.* **2002**, *21*, 137. (d) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413. (e) Bent, S. F. *J. Phys. Chem. B* **2002**, *106*, 2830. (f) Waltenburg, H. N.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 1589.