# Functionalization of the C(100) 2 × 1 Surface by 1,3-Dipolar Cycloadditions: A Theoretical Prediction

### Xin Lu,* Xin Xu, Nanqin Wang, and Qianer Zhang

*State Key Laboratory for Physical Chemistry of Solid Surfaces, Institute of Physical Chemistry, Department of Chemistry, Xiamen University, Xiamen 361005, China*

*Received: January 17, 2002; In Final Form: April 5, 2002*

We present a theoretical prediction of the facile 1,3-dipolar cycloadditions onto the diamond (100) surface, a new type of surface reaction that can be used to functionalize diamond surface at a low temperature.

Diamond is promising as an electronic-device material.[1,2] The chemical modification of diamond surfaces might introduce new physical and chemical properties for specific applications.[3,4] Indeed, it was found that incorporation of nitrogen into the diamond lattice affects its thermal conductivity, optical transparency, hardness, and band gap.[1−5] In this paper, we present a theoretical prediction of the facile 1,3-dipolar cycloaddition of an organic azide (methyl azide) and a diazo compound (diazomethane) onto the diamond (100) surface, a new type of surface reaction that can be used to functionalize diamond surface.

The C(100) 2 × 1 surface has a bonding motif that pairs of atoms form dimers with an ethylene-like double bond.[6,7] This implies that the chemistry of C(100) might show some similarity to the chemistry of alkenes. Due to the nonplanar geometry on the surface dimer, the $\pi$-bonding in the surface dimer is weaker than in ethylene, giving rise to higher reactivity on the surface dimer.[8] Indeed, conjugated dienes (e.g., 1,3-butadiene) can undergo Diels−Alder reaction more easily with C(100) surface than with ethylene, as revealed both experimentally[9,10] and theoretically.[11,12] We noticed that in organic chemistry another famous pericyclic reaction is the 1,3-dipolar cycloaddition (1,3-DC) reaction[13] between a 1,3-dipolar molecule, e.g., azides, and a dipolarophile, in which the dipolarophile can be an alkene, e.g., ethylene, or a molecule containing C=N, C=S, or C=O double bonds. Analogous reactions have been successfully applied in the functionalization of highly conjugated fullerenes (e.g., $C_{60}$ and $C_{70}$).[14,15] On the other hand, a recent theoretical work predicted the readiness of 1,3-DC on Si(100) surface.[16] Inspired by these chemical precedents, we infer that a similar reaction could take place on the C(100) 2 × 1 surface between an in-coming 1,3-dipolar molecule and surface dimer. This new type of surface reaction, if facile, can be used to functionalize the C(100) surface with a wide variety of 1,3-dipolar molecules, such as organic azides (e.g., $CH_3N_3$), diazo compounds (e.g., $CH_2N_2$), nitrile oxide (HCNO), nitro compounds (e.g., $CH_3$-$NO_2$), and nitrile ylide ($HCNCH_2$), etc.

To confirm the inference above, we performed density functional cluster model calculations concerning the 1,3-DC reactions of two representative 1,3-dipolar molecules, methyl azide ($CH_3N_3$) and diazomethane ($CH_2N_2$), on the C(100) surface. A $C_9H_{12}$ cluster was employed to model a dimer site on the C(100) surface. This surface model was used previously in the theoretical studies of the Diels−Alder reactions on the

* Corresponding author. Tel: +86-592-2181600. Fax: +86-592-2183047. E-mail: xinlu@xmu.edu.cn.

**TABLE 1: The Reaction Energies $\Delta E_r$ and Energy Barriers $\Delta E_a$ (kcal/mol) of the 1,3-DC of $CH_3N_3$ and $CH_2N_2$ to the $C_9H_{12}$ Surface Model and $C_2H_4$ (calculated at the B3LYP/6-31+G* level)**

| | $C_9H_{12}$ | | $C_2H_4$ | | | |
|---|---|---|---|---|---|---|
| | $\Delta E_r$ | $\Delta E_a$ | $\Delta E_r$ | $\Delta E_a$ | $\Delta E_{rr}{}^a$ | $\Delta E_{aa}{}^b$ |
| $CH_3N_3$ | −69.7 | 5.7 | −22.9 | 17.7 | 46.8 | 12.0 |
| $CH_2N_2$ | −75.1 | 5.3 | −30.1 | 16.1 | 45.1 | 10.8 |

$^a$ $\Delta E_{rr} = \Delta E_r(C_2H_4) - \Delta E_r(C_9H_{12})$. $^b$ $\Delta E_{aa} = \Delta E_a(C_2H_4) - \Delta E_a(C_9H_{12})$.

C(100) 2 × 1 surface.[11,12] All calculations were performed using the Gaussian94 program.[17] The hybrid density functional B3LYP method[18,19] and the standard 6-31+G* basis sets were employed. It has been shown in the previous theoretical studies that the B3LYP approach with a basis set of double-$\zeta$ quality plus polarization functions can provide a reliable description for the gas-phase 1,3-DC reactions with the B3LYP-predicted energy barriers and reaction enthalpies agreeing well with those obtained by the reliable but more expensive CCSD(T) method.[20,21] The recent theoretical investigation on the Diels−Alder reactions of conjugated dienes onto the C(100) 2 × 1 surface also demonstrated that the difference in the reaction energetics predicted by the B3LYP method and the wave function-based G3(MP2) approach is marginal with the B3LYP-predicted reaction barrier being slightly higher than the G3(MP2)-predicted value.[12] Geometry optimizations were performed with no constraints. Reported energy parameters are zero-point corrected by including the unscaled zero-point-energy (ZPE) calculated at the B3LYP/6-31+G* level. To compare the surface reactions with their gas-phase analogues, the 1,3-DC reactions of the two 1,3-dipoles with ethylene were also studied at the same level of theory. The calculated reaction energies and barrier heights are given in Table 1. Figure 1 shows the calculated reaction pathway for the reaction of $CH_3N_3$ onto the $C_9H_{12}$ surface model, along with the optimized geometries of local minima and transition states.

For methyl azide, the 1,3-DC is highly exothermic by −69.7 kcal/mol predicted at the B3LYP/6-31+G* level. The 1,3-DC product, LM1, is 1,2,3-triazole-like with a five-member ring. The two forming C−N bond lengths are 1.45 and 1.47 Å, respectively. In accord with its high exothermicity, the 1,3-DC process has an early transition state, TS1, in which the two forming C−N bond lengths are 2.58 and 2.44 Å, respectively. The barrier height at TS1 is 5.7 kcal/mol predicted at the B3LYP/6-31+G* level. At the same level of theory, the barrier

Functionalization of the C(100) 2 × 1 Surface

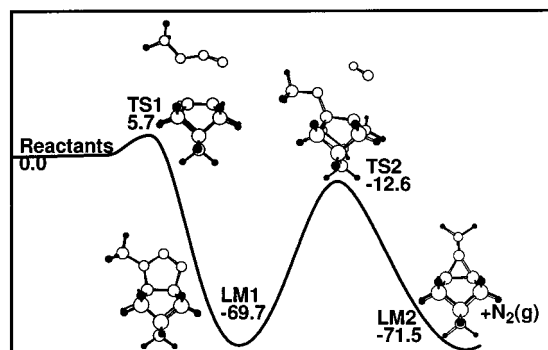*J. Phys. Chem. B, Vol. 106, No. 23, 2002* **5973**



**Figure 1.** Calculated reaction pathway for the 1,3-DC of methyl azide on the $C_9H_{12}$ surface model (relative energies in kcal/mol).

height and reaction energy for the 1,3-DC of methyl azide with ethylene are predicted to be 17.7 kcal/mol and −22.9 kcal/mol, respectively. Hence, the surface reaction has lower activation barrier and exothermicity than those of its molecular analogue. The easiness of the surface reaction can be attributed to the weaker $\pi$-bonding in the surface dimer than in ethylene. Note that the $\pi$-bond strength on C(100) ($\sim$11−21 kcal/mol)[22] is by $\sim$40−50 kcal/mol smaller than that for a typical alkene ($\sim$60 kcal/mol).[23] Interestingly, the difference in the formation energy of the surface product and the molecular product is 46.8 kcal/mol, in accordance with the very difference in $\pi$-bond strength.

Cluster size effect has been further considered for the surface 1,3-DC of methyl azide by using a larger $C_{21}H_{22}$ cluster model, which has three surface dimers in the same dimer row.[11] With this large cluster, the reaction energy and barrier height predicted at the B3LYP/6-31+G* level are −64.0 and 5.7 kcal/mol, respectively, agreeing quite well with those obtained by using the $C_9H_{12}$ cluster model.

The 1,3-DC of diazomethane onto the $C_9H_{12}$ surface model is also highly exothermic. The predicted reaction energy is −75.1 kcal/mol. The product has a five-member ring, in which the forming N−C and C−C bond lengths are 1.47 and 1.52 Å, respectively. An early transition state was located with a barrier height of 5.3 kcal/mol and the forming N−C and C−C bond lengths of 2.70 and 2.54 Å, respectively. Similar to the methyl azide case, the activation energy and exothermicity of this reaction are lower than those for the analogous gas-phase reaction. For the molecular reaction between diazomethane and ethylene, the reaction energy and the barrier height predicted at the B3LYP/6-31+G* level are −30.1 and 16.1 kcal/mol, respectively. The difference between the reaction energies of the surface reaction and its molecular analogue is 45.1 kcal/mol, similar to the methyl azide case.

In molecular reactions, one feature of 1,3-DC is that the 1,3-DC products of methyl azide (or diazomethane) with alkenes sometimes may not be very stable and can further undergo elimination of $N_2$.[13,24] Accordingly, for the surface reaction of methyl azide, we have also considered the possibility of $N_2$ elimination from the as-formed 1,2,3-triazole-like surface species (LM1). As shown in Figure 1, elimination of $N_2$ from LM1 requires an activation energy of $\sim$57 kcal/mol, but the transition state (TS2) is by 12.6 kcal/mol lower than the initial reactants ($CH_3N_3 + C_9H_{12}$) in energy. This suggests that the elimination of $N_2$ from 1,3-DC products may readily occur at elevated temperature. The final product is an $NCH_3$(a) adspecies, which is di-$\sigma$ bonded to the surface dimer forming a C−N−C three-member ring.

Apart from the above-concerned methyl azide and diazomethane, we are undertaking a systematic theoretical study

regarding the 1,3-DC reactions of a variety of 1,3 dipolar molecules with the diamond (100) surface. Preliminary work indicated that the 1,3-DC reactions of nitrile ylide and nitrile oxide on C(100) 2 × 1 surface are even more exothermic than that of diazomethane, which provides further evidence of the facile 1,3-DC on C(100) 2 × 1 surface.

In summary, we predicted, on the basis of chemical precedents and quantum chemical calculations, the facile 1,3-DC of methyl azide and diazomethane onto the C(100) 2 × 1 surface. The surface reactions have lower activation energies and exothermicities than those of their molecular analogues. So far we are not aware of any experimental or theoretical work prior to the present one regarding this type of reaction on the diamond (100) surface. This new type of surface reaction in combination with the wide variety of 1,3-dipolar molecules provides high flexibility of functionalizing and fabricating the diamond films at a low temperature. To this end, further experimental and theoretical efforts are needed. Furthermore, the known successes in functionalizing the highly conjugated fullerenes[14,15] and the diamond (100) surface[8,9] by means of synthetic organic chemistry inspire us with the possibility of chemically modifying the highly conjugated carbon nanotubes by means of synthetic organic chemistry.

**Supporting Information Available:** Optimized geometries for the reactants, transition states, and products of the $CH_3N_3$ and $CH_2N_2$ reactions with the $C_9H_{12}$ surface model are presented in Figure 2 and Figure 3, respectively. The material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**

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

(2) Nakahata, H.; Imai, T.; Fujimori, N. *Diamond Materials*, Proc. Vol. 91−98; The Electrochemical Society, Pennington, NJ, 1991; p 487.

(3) Grot, S. A.; Gildenblat, G. Sh.; Hatfield, C. W.; Wronski, A. R.; Badzian, A. R.; Badzian, T.; Messier, R. *IEEE Elect. Dev. Lett.* **1990**, *11*, 100.

(4) Niu, C.; Lu, Y. Z.; Lieber, C. M. *Science* **1993**, *261*, 334.

(5) Liu, A. Y.; Cohen, M. L. *Science* **1989**, *245*, 841.

(6) Krüger, P.; Pollmann, J. *Phys. Rev. Lett.* **1995**, *74*, 1155.

(7) Furthmüller, J.; Hafner, J.; Kresse, G. *Phys. Rev. B* **1996**, *53*, 7334.

(8) Hovis, J. S.; Coutler, S. K.; Hamers, R. J.; D'Evelyn, M. P.; Russell, J. N., Jr.; Butler, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 732.

(9) Hossain, M. Z.; Aruga, T.; Takagi, N.; Tsuno, T.; Fujimori, N.; Ando, T.; Nishijima, M. *Jpn. J. Appl. Phys.* **1999**, *38*, L1496.

(10) Wang, G. T.; Bent, S. F.; Russell, J. N., Jr.; Butler, J. E.; D'Evelyn, M. P. *J. Am. Chem. Soc.* **2000**, *122*, 744.

(11) Fitzgerald, D. R.; Doren, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 12334.

(12) Okamoto, Y. *J. Phys. Chem. B* **2001**, *105*, 1813.

(13) *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1.

(14) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.

(15) Cases, M.; Duran, M.; Mestres, J.; Martin, N.; Sola, M. *J. Org. Chem.* **2001**, *66*, 433, and references therein.

(16) Barriocanal, J. A.; Doren, D. J. *J. Vac. Sci. Technol. A* **2000**, *18*, 1959.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, *Revision B.3*; Gaussian, Inc: Pittsburgh, PA, 1995.

(18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(19) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. A* **1988**, *37*, 785.

(20) Houk, K. N.; Wiest, O. *Top. Curr. Chem.* **1996**, *183*, 1.

(21) Su, M. D.; Liao, H. Y.; Chung, W. S.; Chu, S. Y. *J. Org. Chem.* **1999**, *64*, 6710.

(22) Hukka, T. J.; Pakkanen, T. A.; D'Evelyn, M. P. *J. Phys. Chem.* **1994**, *98*, 12420.

(23) Janz, G. J. *Thermodynamic Properties of Organic Compounds*; Academic Press, New York, 1967.

(24) Gillette, G. R.; West, R. *J. Organomet. Chem.* **1990**, *394*, 45.