

The surface-radical–surface-olefin recombination step for CVD growth of diamond. Calculation of the rate constant from first principles

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Abstract

Recombination of a surface-radical with a surface-olefin (SR-SOR) to form a six-membered ring is a critical step in the current mechanism for chemical vapor deposition growth of the diamond (100) surface. We estimate the rate constant for SR-SOR by combining quantum chemistry calculations, molecular mechanics calculations, and transition state theory. The ab initio calculations include extensive electron correlation (MP2 and GVB* SD CI) on cluster models which were corrected for steric interactions of the cluster with the rest of the surface and for strain effects on the lattice. The ab initio vibrational frequencies, which were used to construct a partition function for calculating the entropy, were calculated at the MP2 level. Transition state theory was used to obtain the rate constant, $k = 5.6 \times 10^{12} e^{-8800/RT} \text{ s}^{-1}$. This implies that under normal growth conditions SR-SOR is fast compared to competing gas–surface reactions.

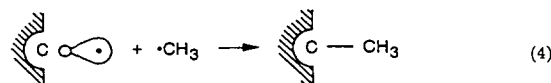
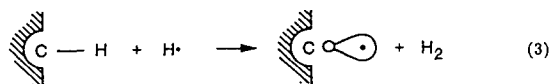
1. Introduction

Because of strong industrial interest in developing low-pressure technologies for synthesizing diamond, there has been considerable effort in elucidating the fundamental mechanisms of diamond film growth [1–3]. Since the kinetics and thermochemistry of carbon–hydrogen systems are well known, the chemical vapor deposition (CVD) of diamond is probably the best candidate for understanding CVD at a detailed level.

A number of experiments have shown that methyl radicals are generally the dominant gas phase precursor species reacting with the surface to grow diamond [4–8], and several detailed chemical kinetics mechanisms have been proposed to analyze growth on various idealized diamond surfaces [9–16]. The overall process is given by

$$\text{H}_2 \rightarrow 2\text{H}^\bullet, \quad (1)$$

$$\text{CH}_4 + \text{H}^\bullet \rightarrow \text{CH}_3^\bullet + \text{H}_2, \quad (2)$$



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For tetrahedral electronic materials (Si, GaAs, ...) the (100) surface has generally been the surface of interest for commercial growth of thin films by CVD and MBE technology. Hence the mechanisms for diamond growth on this surface are of interest. Both AFM and STM measurements have established that the stable surface is hydrogen terminated with a 2×1 reconstruction as indicated in Fig. 1. A close-up of the five-membered rings (denoted as C_5) is shown in Fig. 2a. This C_5 ring must be opened and converted to a six-membered ring (C_5 to C_6) during growth. The Garrison–Brenner dimer mechanism has been proposed to explain this process, and it has been analyzed in terms of known rates for analogous gas phase hydrocarbon reactions. One step in this reaction, namely the surface-radical–surface-olefin recombination (SR-SOR) step, involves surface constraints that preclude using estimates from gas phase reactions. In this Letter we report extensive *ab initio* calculations, including electron correlation, to examine this step. We conclude that the rate is fast enough

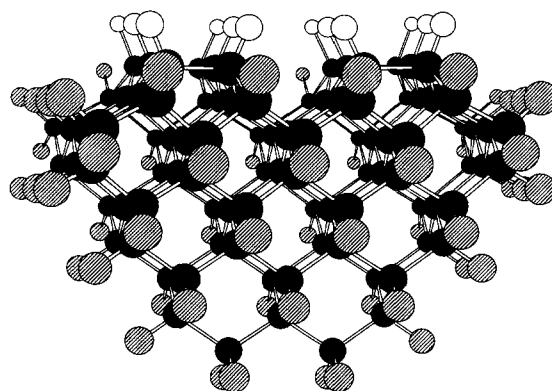


Fig. 1. Dimer paired structure of the H stabilized C(100) surface; unshaded = H, shaded = bulk C, hatched = bulk terminating C.

to be consistent with the Garrison–Brenner mechanism.

In Section 2 we review the Garrison–Brenner mechanism. Section 3 discusses the details of the calculation, culminating in a rate constant for the

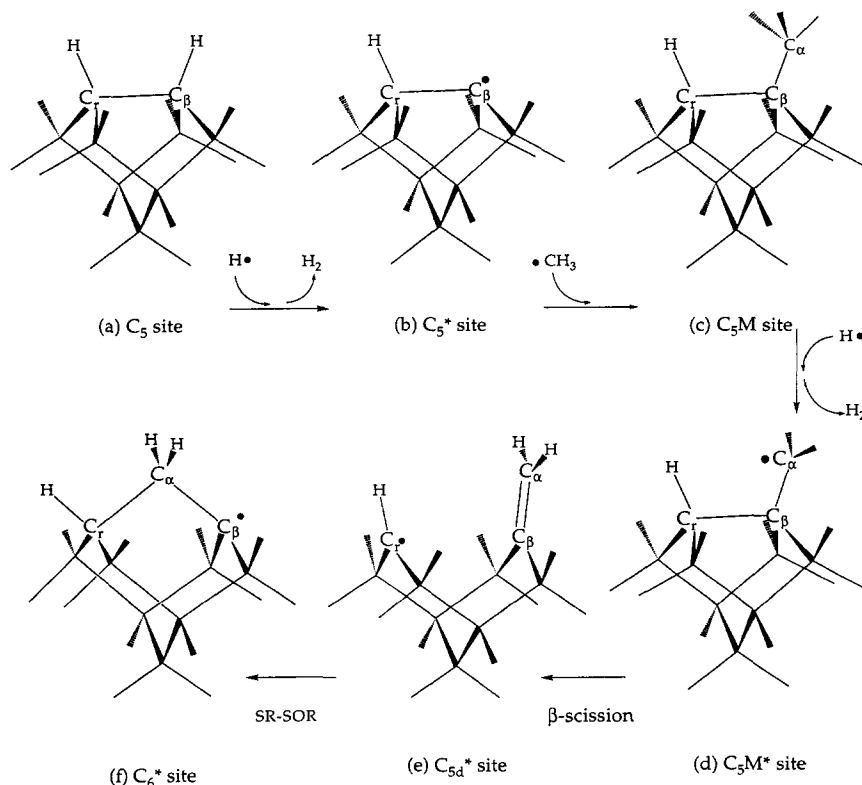


Fig. 2. The Garrison–Brenner mechanism for dimer ring opening during CVD growth of C(100).

SR-SOR step. Section 4 discusses the relation to other rates involved in diamond growth.

2. The mechanism

The Garrison–Brenner [5] dimer mechanism sketched in Fig. 2 was based on molecular dynamics simulations (using the Brenner hydrocarbon potential [17]) and has been analyzed in detail by Harris and Goodwin [15].

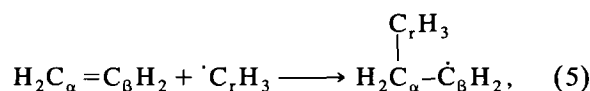
(i) It commences with addition of a CH_3 radical to a surface radical site (Fig. 2b–2c), forming the structure denoted as C_5M .

(ii) The next step (Fig. 2c–2d) is abstraction of a hydrogen atom from the CH_3 group to make the radical denoted as C_5M^* .

(iii) Through the β -scission electronic rearrangement (Fig. 2d–2e), this structure isomerizes to another radical, denoted as C_{5d}^* . Here the dimer bond breaks and a double bond forms between the carbon atom (C_β) of the original structure and the carbon atom (C_α) that started as an adsorbed methyl (now the α -carbon of the olefin). Such unimolecular reactions are generally fast compared with bimolecular reactions.

(iv) The final SR-SOR step in the mechanism (Fig. 2e–2f) is intramolecular attack of the radical carbon (C_r) of C_{5d}^* with the C_α of the double bond. This leads to a six-membered ring denoted as C_6^* , containing a radical site (C_β). It is this step that we examine herein.

Gas phase reactions involving radical attack at a doubly bonded carbon, such as



are typically very fast and proceed with almost no barrier. However, on the surface two factors considerably decrease the rate:

(i) the initial equilibrium distance between the radical carbon, C_r , and the α -carbon, C_α , is 2.85 Å, almost twice the normal CC bond distance, and

(ii) C_r is tightly constrained by the lattice from moving toward C_α , while moving C_α toward C_r bends the bonds C_β to the lattice or makes the bonds at C_β nonplanar, leading to strain.

Thus, on the growing diamond surface the SR-SOR reaction step



could have a significant barrier, which might make the constrained SR-SOR reaction (6) sufficiently slow on the diamond surface as to limit the rate of diamond formation.

3. Computational details

3.1. Ab initio quantum chemistry

In order to obtain accurate potential energy surfaces for reactions such as (5) or (6), it is essential to include all electron correlation effects that change during the reaction. For this purpose we use the generalized valence bond (GVB) method [18], in which all electrons involved in bonds that change during the reaction are fully correlated (these are the active electrons), and all other pairs of electrons are calculated self-consistently (the semi-active electrons). For reactions (5) and (6) there are three such active electrons. For the reactant these correspond to the electrons of the π -bond ($\text{C}_\alpha=\text{C}_\beta$) and the radical electron of C_r . In the product they correspond to the two electrons of the new C–C σ -bond ($\text{C}_r-\text{C}_\alpha$) and the radical electron on C_β . There are two ways to spin pair these three electrons (one corresponding to reactant and the other to the product) and the GVB method calculates all orbitals self-consistently (these three plus the orbitals for all other electrons) while optimizing the spin coupling [19]. This type of calculation is also referred to as complete active space-self-consistent field (CASSCF). After calculating the GVB wavefunction, we then allow all single and double excitations from the three GVB configurations to all possible virtual orbitals, GVB*SD CI. This accurately approximates the results of very complete CI calculations [20]. A second approach (MP2) starts with the Hartree–Fock wavefunction and uses second-order (Møller–Plesset) perturbation theory to include the dominant many-body effects [21].

To describe the reaction path we considered 40 positions of the critical carbon, C_α , selected to de-

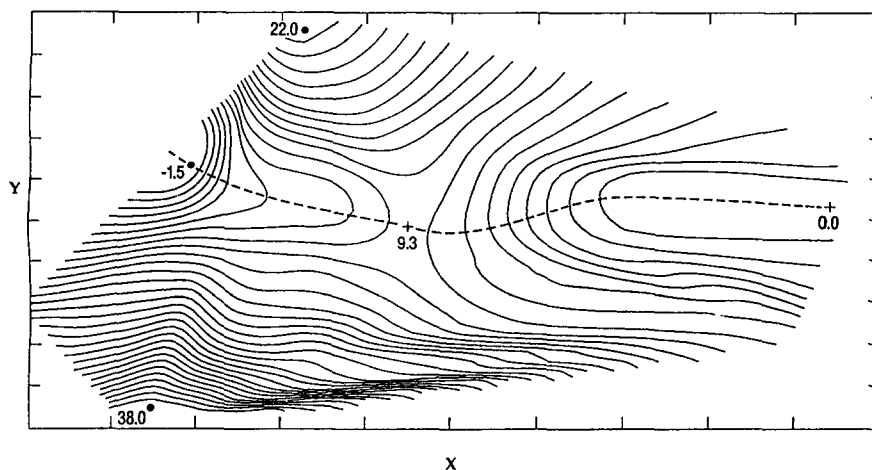


Fig. 3. The energy surface for the SR-SOR reaction from GVB-SD CI calculations. The reactant site is denoted as 0.0. The saddle point for the reaction is denoted as 9.3. The product is far to the left and top of the figure with an energy of -35.1 kcal/mol. The contour spacing is 1.25 kcal/mol. The coordinates X and Y are the Cartesian coordinates for motion of C_α parallel (X) and perpendicular (Y) to the surface while remaining in the (110) plane of the crystal which contains C_r and C_β . Tick marks are 0.1 and 0.05 Å in the x and y directions, respectively.

scribe the reactant, saddle point, and product states. We fixed C_r , C_β and the bonds to C_r and on C_β representing the bulk atoms. Then for each position of C_α , we optimized at the MP2 level the position of the three hydrogens. For each such geometry from MP2, we calculated the GVB-CI and GVB*SD CI energies.

The above calculations were carried out using the C_3H_7 cluster obtained from Fig. 2e by using H's to represent the subsurface carbons (keeping the same angles). We also performed ab initio calculations on the $C_{10}H_{15}$ cluster shown in Fig. 2e and obtained from Fig. 1 by using hydrogens to represent the subsurface (shaded) carbons. This allowed us to estimate the effects of cluster size on the reaction barriers by considering (i) the reactant geometry, and (ii) the transition state geometry. In these later calculations, the positions of C_r , C_α , and C_β and the three hydrogen atoms bonded to these carbon atoms were all optimized, giving a better model for relaxation of the surface. The remaining seven carbon atoms and twelve hydrogen atoms were held fixed to model the lattice. This optimization was carried out at the MP2 level of Møller–Plesset perturbation theory [21]. Using the MP2 optimized geometries, we carried out the GVB-CI calculations to obtain the barrier.

For all GVB calculations on the three-carbon

cluster we used the Dunning/Huzinaga double ζ basis set [22,23] plus diffuse s and p functions ($\zeta^s = 0.0474$, $\zeta^p = 0.0365$) plus one set of d polarization functions ($\zeta = 0.75$). The triple zeta contraction of the 6s basis was used for hydrogens. The 6-31G** basis set was used for the MP2 optimizations on the three-carbon cluster while 6-31G* was used for the MP2 optimizations on the ten-carbon cluster. MP2 was performed using GAUSSIAN 92 [24]. The HF, GVB-CI, and GVB*SD CI calculations used the GVB [25]¹ and MOLECULE SWEDEN suites of programs [27].

3.2. Potential surface

Using the energies from GVB*SD CI and MP2 calculations, we determined the potential energy surface shown in Fig. 3 (the reaction path is shown by the dashed curve). The calculated reaction barrier generally falls with increasing levels of correlation. Thus,

$$E_{\text{act}}^{\text{HF}} = 18.1 \text{ kcal/mol},$$

¹ See Ref. [26].

$$E_{\text{act}}^{\text{MP}2} = 10.0 \text{ kcal/mol},$$

$$E_{\text{act}}^{\text{GVB-Cl}} = 10.5 \text{ kcal/mol}, \text{ and}$$

$$E_{\text{act}}^{\text{GVB} \cdot \text{SDCI}} = 9.3 \text{ kcal/mol}.$$

Hartree–Fock (HF) leads to a barrier about a factor of two too high and to a poor location of the transition state geometry. The $E_{\text{act}} = 9.3 \text{ kcal/mol}$ from the GVB*SD CI is expected to be about 1 kcal/mol too high from residual errors due to incompleteness of the basis set and the CI expansion (see Table 1). Thus for the SR-SOR process, we obtain a corrected GVB*SD CI activation barrier of

$$E_{\text{act}}^{\text{exact}} \approx 8.3 \text{ kcal/mol}.$$

We calculated the zero point energy contribution to the vibrational adiabatic barrier by computing the MP2 vibrational frequencies at the transition and initial states. This adds 0.13 kcal/mol to the activation barrier, leading to

$$E_{\text{cluster}}^{\text{act}} \approx 8.4 \text{ kcal/mol}. \quad (7)$$

3.3. Molecular mechanics calculations

The strain energy imposed on the lattice by the reacting surface species was calculated with molecular mechanics using the MSXX many-body force field (fit to the phonon dispersion curves and elastic constants of diamond [28]). To model the SR-SOR reaction we increased the cubic unit cell by a factor of 4 in the z direction and by factors of 5 in the x and y directions (leading to 800 atoms in the unit cell). We then cleaved the (001) surface [28], leading to a slab which was then hydrogenated. The cluster atoms optimized in the quantum chemistry calculations were held fixed at the initial, final, and transition state geometries, while the remaining atoms of the slab were optimized [28]. Strains and steric interactions included in the ab initio cluster calculations were not included in the molecular mechanics energy to avoid double counting of this portion of the energy. Cell structure and atomic coordinates were updated at each optimization cycle. The atomic coordinates were optimized² using conjugate gradient

Table 1

Contributions to the activation energy for the SR-SOR step

Calculation	Energy (kcal/mol)
quantum chemical calculations	
GVB*SD CI	9.30
corrections (basis set and correlation)	– 1.0
differential zero point energy	0.13
net electronic structure barrier	8.43
force field calculations	
strain from balance of surface	0.73
van der Waals interactions	– 0.34
total E_{act}	8.82

techniques until the RMS force per degree of freedom was less than 0.01 (kcal/mol)/Å. The lattice strain energy (not including van der Waals interactions) and the van der Waals energy were calculated for the transition state and the reactant state. These energies do not include the interactions already included in the ab initio calculations on the cluster. The steric interactions with the surrounding lattice *decreases* in the transition state relative to the initial state. The strain imposed on the lattice at the transition state relative to the reactant state is calculated to add 0.73 kcal/mol to the barrier while the van der Waals interactions subtract 0.34 kcal/mol from the barrier. Thus these effects increase the net electronic structure barrier by 0.39 kcal/mol to yield a net barrier of

$$E_{\text{act}}^{\text{surface}} = 8.8 \text{ kcal/mol}. \quad (8)$$

3.4. Transition state theory

We determined the entropy change $\Delta S^\ddagger$ between reactants and the transition state from vibrational mode analyses that included the effects of the constraints on the vibrational levels during the reaction. First, the Hessian (second derivative matrix) was calculated using MP2 theory at each geometry of the C_3H_4 cluster [24]. Next, the $3N - 6$ vibrational levels were calculated by diagonalizing the (mass-weighted) Hessian (see footnote 2). Finally, these energy levels were used to construct a partition function from which the entropy was calculated (see

² These calculations used POLYGRAF from Molecular Simulations Inc. (Burlington, MA).

footnote 2). For the transition state the imaginary vibrational frequency was ignored.

The TST pre-exponential factor is given by

$$A = \frac{ek_{\text{B}}T}{h} \exp(\Delta S^{\ddagger}/R), \quad (9)$$

where $\ln e = 1$, k_{B} is the Boltzmann constant, T is the temperature, h is the Planck constant, R is the gas constant, and $\Delta S^{\ddagger}$ is the change in entropy between C_d^* and the transition state. We estimated the entropies for the initial, transition, and final states of reaction (6), leading to $\Delta S^{\ddagger} = -2.6$ cal/mol K and

$$A = 5.6 \times 10^{12} \quad (10)$$

at 1000 K from Eq. (9).

Combining (8) with (10) leads to a total rate constant for SR-SOR of

$$k_{\text{SR-SOR}} = 5.6 \times 10^{12} \text{ e}^{-8800/RT} \text{ s}^{-1}. \quad (11)$$

4. Discussion

The unimolecular reaction (6) on the diamond surface competes primarily with abstraction and addition reactions involving gas phase H atoms. To examine the relative importance of these competing gas phase reactions, we compare reaction (6) with reaction (12),



in which the radical site recombines with a gas phase H atom. At 1200 K the characteristic time scale for (6) is $1/k_{\text{SR-SOR}} = 7 \times 10^{-12}$ s. In contrast, assuming k_{12} is in the range [29] 10^{13} to 10^{14} cm³/mol s with a H atom concentration [29] of 10^{-10} – 10^{-6} atoms/cm³, leads to characteristic time scales of 10^{-3} to 10^{-8} s. Thus the SR-SOR reaction is 10^4 – 10^9 times faster than other steps in the growth process, indicating that it does not affect the rate of diamond growth in the Garrison–Benner mechanism.

Reactions like SR-SOR may also occur at steps or edges and can play a role for the (111) and reconstructed (110) surfaces. At such sites the surface constraints may place the initial structure for the SR-SOR step either closer or farther from the transi-

tion state, resulting in changes in strain that could decrease or increase the barrier relative to that reported here.

It has been speculated [30] that SR-SOR might also be a mechanism for carbon incorporation in GaAs and Si. Because of differences in stability of various sp^n structures [31] for C relative to Si, Ga, and As, such case could have dramatically modified barriers.

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