Radical Rearrangements for the Chemical Vapor Deposition of Diamond

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A combination of chemical trapping and computations is used to determine the activation parameters for the interconversion of the 3-methylenebicyclo[3.3.1]nonan-7-yl (**1**), (3-noradamantyl)methyl (**2**), and 1-adamantyl (**3**) radicals. The three radicals model proposed intermediate surface radical structures in the chemical vapor deposition (CVD) of diamond on its 2 × 1 reconstructed [100] surface. The study finds that relatively low-level calculations previously applied to the problem of diamond growth are reliable, at least qualitatively.

Introduction

The chemical vapor deposition (CVD) of diamond has become an established technology for the production of polycrystalline diamond for a variety of technical applications.[1,2] Experimental studies on the effect of macroscopic process variables, e.g., temperature, pressure, added gases, flow rate, initiation method, etc., have appeared in great number and contributed to the long, incremental improvement in both the growth rate and quality of CVD diamond. The chemical mechanism, however, by which C_1 and/or C_2 units are incorporated into a new layer of diamond lattice, has received less scrutiny, with computational, and a few experimental, studies appearing in recent years.[3,4] Even those experimental studies that have been done purport only to identify the important gas-phase carbon-containing precursors to diamond on the surface.[5] There are no experiments pertaining to the structural transformation on a microscopic level. One may suppose that a better-than-incremental advance in the art will require at least some mechanistic information on the surface reactions of diamond.

Of the several mechanisms proposed in the literature, one based on the 5-hexenyl rearrangement appears most plausible from the viewpoint of an organic chemist. The 5-hexenyl rearrangement, a "radical clock" reaction,[6] has been extensively investigated (Scheme 1). The proposed mechanism[8,9] for diamond growth from H• and •CH$_3$ in a

Scheme 1. 5-Hexenyl Radical and the Two Modes for Cyclization Using Baldwin's Designations
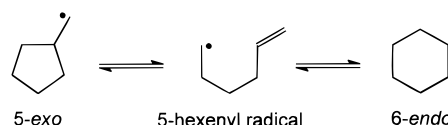
CVD reactor by way of this rearrangement is shown in Scheme 2, starting from a 2 × 1 reconstructed [100] surface believed to be an important starting point for growth.[3] Notice that the carbon atom in the methyl group external to the crystal is incorporated into the framework.

The basic steps are as follows: (i) hydrogen abstraction from a 2 × 1 reconstructed [100] surface by H•, (ii) coupling of a methyl radical with the surface radical site, (iii) abstraction of a hydrogen from the pendant methyl group, (iv) ring-opening to generate the 5-hexenyl radical, (v) ring-closure by radical addition to the other end of the olefinic unit, and (vi) 1,5-hydrogen translocation. The same basic rearrangement suffices to "shuffle" bridge sites together to form the experimentally observed smooth surfaces. Of these steps, only the 2 × 1 reconstruction itself should require elevated temperatures. The remaining steps are all well-known for simpler organic systems in solution and should proceed rapidly at temperatures substantially below these in typical CVD reactions. Accordingly, while the gross kinetics of diamond growth in CVD at 1200 K are probably not greatly affected by differences in activation energies for the surface rearrangements, i.e., the surface rearrangements are not rate-limiting,[9] an accurate knowledge of the energetics for the surface chemistry is nevertheless important as one begins to design analogous processes that run at much lower temperatures. Lower temperature operation would be advantageous in the production of a technologically important material like diamond and provides the motivation for the present work. Lastly, it should be emphasized that, even if the proposed 5-hexenyl mechanism is operative in only some instances for CVD, the simplicity of the chemistry makes this mechanism important to designed processes that will generate diamond

(1) For a review of properties and production of CVD diamond, see: Yarbrough, W. A.; Messier, R. *Science* **1990**, *247*, 688.

(2) Derjaguin, B. V.; Fedoseev, D. V.; Lukyanovich, V. M.; Spitsyn, B. V.; Ryabov, V. A.; Lavrentyev, A. V. *J. Cryst. Growth* **1968**, *2*, 380. Eversole, W. G. U.S. Patent 3,030,188, 1961. Angus, J. C.; Will, H. A.; Stanko, W. S. *J. Appl. Phys.* **1968**, *39*, 2915. Angus, J. C. U.S. Patent 3,630,677, 1971.

(3) For a review of terminology, surface morphology, and growth mechanisms, see: Butler, J. E.; Woodin, R. L. *Phil. Trans. R. Soc. London A* **1993**, *342*, 209.

(4) Harris, S. J.; Goodwin, D. G. *J. Phys. Chem.* **1993**, *97*, 23. Zhu, M.; Hauge, R. H.; Margrave, J. L.; D'Evelyn, M. P. *Proc. 3rd Int. Symp. Diamond Mat.* **1993**, 138. Harris, S. J. *Appl. Phys. Lett.* **1990**, *56*, 2298.

(5) Lee, S. S.; Minsek, D. W.; Vestyck, D. J.; Chen, P. *Science* **1994**, *263*, 1596.

(6) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(7) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734, 736, 738.

(8) Garrison, B. J.; Dawnkaski, E. J.; Srinivasta, D.; Brenner, D. W. *Science* **1992**, *255*, 835.

(9) Shokov, S.; Weiner, B.; Frenklach, M. *J. Phys. Chem.* **1994**, *98*, 7073.

Scheme 2.   Proposed Mechanism for Diamond Growth on a 2 × 1 Reconstructed [100] Surface with Atomic Hydrogen and Methyl Radicals, Adapted from Refs 8 and 9 (Descriptions of Each Step Are in the Text)
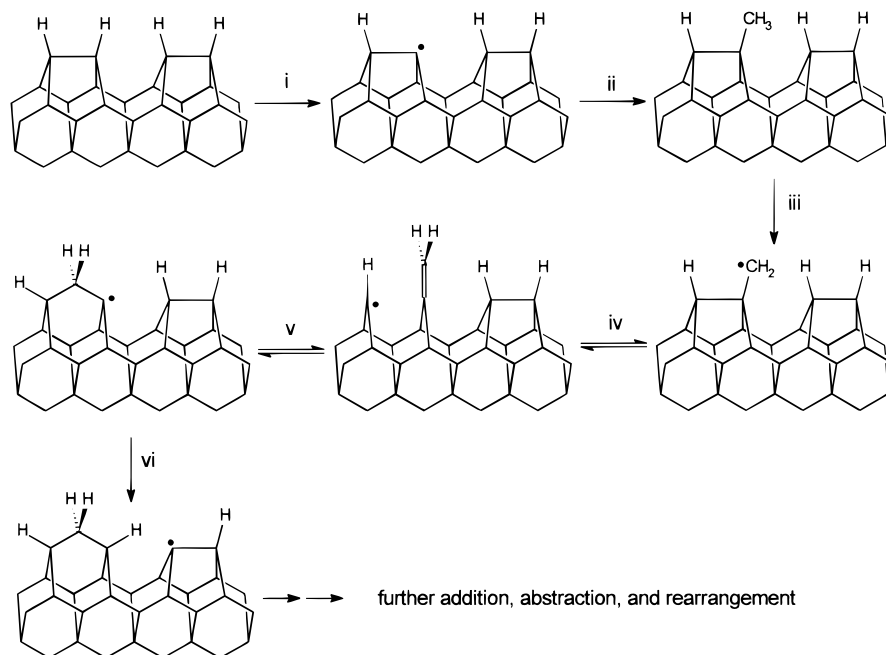
by non-CVD reaction sequences that mimic the high-temperature chemistry in CVD.

In the present report, we show a combination of experimental and computational results on a set of 5-hexenyl radical rearrangements of cage hydrocarbons that model the diamond [100] surface. By preparation of the 3-methylenebicyclo[3.3.1]nonan-7-yl (**1**), (3-noradamantyl)methyl (**2**), and 1-adamantyl (**3**) radicals, competitive trapping of the radicals as a function of temperature, and molecular mechanics modeling of the corresponding hydrocarbons, the relative enthalpies of the three radicals and the transition states for their interconversions are determined.
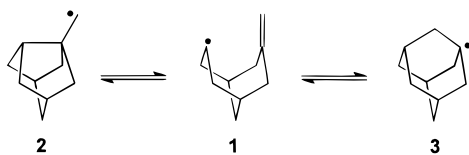

The results are compared to published calculations of the surface reactions on diamond, as well as ab initio computations at a modest level, showing that, while the rearrangements are eminently plausible as basic components in diamond CVD chemistry, the level of theory being currently brought to bear on the problem is quantitatively in error, in particular overestimating activation energies.

Results

The trapping reactions of radicals **1**−**3** in CCl$_4$, generated thermally from the "Barton" precursors prepared in situ, produce 3-methylene-7-chlorobicyclo[3.3.1]nonane (**4**), (3-noradamantyl)chloromethane (**5**), and 1-chloroadamantane (**6**). Two of the three sets of trapping results are relatively uninformative, although they become relevant in light of the third one: From noradamantylmethanol (the direct precursor to **2**), the expected product **5** and the coupling product **7** of thiopyridinyl and trichlo-

Table 1.   Trapping Product Ratios in the Reaction of 1 with CCl$_4$ at Different Temperatures (The Radical Precursor Is Generated In Situ)
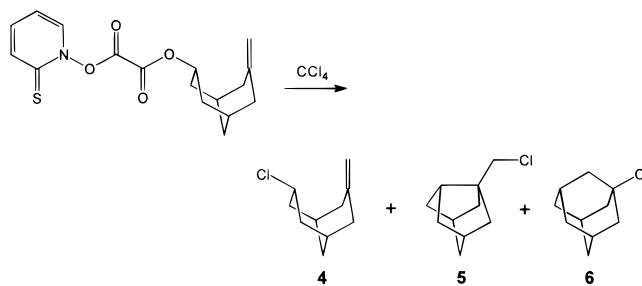
T (°C)	75	98	116	126
%**4** (±0.5)	1.7^a (1.7)	1.3 (1.5)	1.1 (1.4)	0.9 (1.4)
%**5** (±1.0)	96.5^c (96.5)	95.6 (96.2)	95.9 (95.9)	95.6 (95.6)
%**6** (±0.9)	1.8^b (1.8)	3.1 (2.3)	3.0 (2.7)	3.5 (3.0)

^{a} Average of 10 runs. ^{b}Average of two runs. ^{c} Remainder of trapped radical products. The numbers in parentheses are predicted product yields from the kinetic simulation using the final derived kinetic parameters (see Discussion).

romethyl radicals are the only radical products observed in the GC/MS traces. Similarly, from 1-adamantanol (the direct precursor to **3**), the only radical-derived products were **6** and **7**. The most important set of trapping studies starts from methylenebicyclononanol (the direct precursor to **1**), from which all three desired products, **4**−**6**, are formed (at 75 °C), in a combined yield of 72%. Within that total, the product distribution is shown in Table 1.

At temperatures much higher than the 126 °C run, e.g., 135−170 °C, significant decomposition of the CCl$_4$ solvent occurred, which could perturb the product ratios. In general, the measurement of reliable, quantitative product ratios is complicated by a variety of experimental difficulties. For example, the C$_{10}$H$_{15}$Cl compounds with cage structures are surprisingly volatile, so care must be exercised that the workup prior to analysis does not differentially deplete any component by evaporation. Also, one can conceive of a radical chain-induced isomer-

ization of **4** to either **5** or **6** in cases where solvent decomposition produces Cl·. No other products assignable to the radicals **1**−**3** were found in the runs from which kinetic data were extracted. The major side product not derived from the radicals was monobasic acid **8**, formed by hydrolysis of the remaining acid chloride moiety in the monoester between alcohols and oxalyl chloride by trace amounts of water. The total mass balance of the desired products **4**−**6** plus **8** is 91% from the oxalic acid monoester, with the remainder consisting of solvolysis products of the alcohol or products from incomplete decomposition of the oxalate ester. It was very important to the acquisition of reliable product ratios to account for as much of the mass as possible. One should note that any side product coming from the Barton precursor prior to double decarboxylation would have no effect on the relative ratios of **4**−**6** and, thus, no effect on the derived thermochemistry. As a check, we also determined that the products themselves did not interconvert after they were formed by subjecting a 5.3/12.2/82.4 mixture (an arbitrary ratio) of **4**, **5**, and **6** to the reaction conditions. No alteration in the initial ratio was observed. A minor difficulty occurred when it was discovered that small amounts of **6** appeared already after the reaction of methylenebicyclononanol with oxalyl chloride, presumably arising from traces of HCl in the oxalyl chloride. Attempts to suppress the "premature" formation of **6** met with only variable success. We judged it more reliable to correct for existing **6**. GC/MS analysis of an aliquot removed from the reaction immediately prior to addition to the thiopyridine *N*-oxide allowed us to subtract off the spurious contribution to the total chloroadamantane product, which amounted to only a small correction. In the end, the product ratios for **1**−**3** at 75 °C were used to derive absolute rates for the **1** → **2** and **1** → **3** reactions. However, kinetic simulations for higher temperatures, based on the absolute isomerization rates of **1** at 75 °C, will be validated by comparing the projected product ratios at higher temperatures to the measured distributions. The success of that simulation lends credence to the legitimacy of the procedure.

Discussion

A considerable body of data exists for the 5-hexenyl rearrangement, not only because of its preparative importance, but also because of the role of the rearrangement as a "radical-clock" reaction[6] for competitive kinetics in radical reactions. The wealth of experimental results from which qualitative comparisons may be drawn seems to have escaped notice in the CVD kinetics community. While there is general agreement that the 5-exo cyclization of 5-hexenyl radicals is kinetically preferred despite the thermodynamic preference for the 6-endo product, it has been noted that both the kinetic and thermodynamic preferences are strongly dependent on steric and electronic factors.[10] In particular, alkyl substituents at the 5-position in simple 5-hexenyl systems can reverse the kinetic preference from 5-exo to 6-endo cyclization.[11] Given the presence of just such a substitution pattern in the 3-methylenebicyclo[3.3.1]nonan-7-yl structures in the proposed CVD mechanism, reliable predictions ought to be difficult.

Table 2. Product Ratios in the Radical Chain Cyclization of 3,7-Dimethylenebicyclo[3.3.1]nonane with Bromotrichloromethane upon γ Irradiation (From Ref 12)
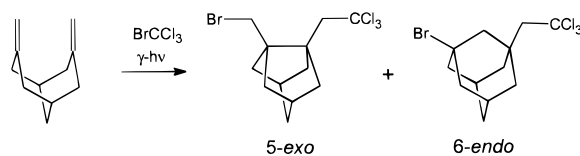
T (°C)	22	40	77	100	150	200
%5-exo	100.0	99.9	97.7	95.4	90.3	44.8
%6-endo	0.0	0.1	2.3	4.6	9.7	55.2

Table 3. Enthalpies, in kcal/mol Relative to the 3-Methylenebicyclo[3.3.1]nonan-7-yl Radical (1), for the (3-Noradamantyl)methyl (2) and 1-Adamantyl (3) Radicals and the Transition States for Their Interconversion

	2	[TS]‡	**1**	[TS]‡	**3**
Ref. [9]	-6.0	10.0	0.0	12.3	-24.0
MP2/6-31G*	-0.2	15.8	0.0	14.8	-14.1
expt.	-9.0 ± 1.5	5.4 ± 1.0	0.0	8.2 ± 1.0	-20.0 ± 2.0

The closest model system for which product studies give some indication of 5-*exo* vs 6-*endo* cyclization preference is 3,7-dimethylenebicyclo[3.3.1]nonane, which in BrCCl₃ with radical chain initiation, gives two adducts (Table 2).[12,13] The product ratios at the higher temperatures are suspect because of the difficulties mentioned earlier, but the general trend is similar. Direct comparison of these data to the computations for diamond CVD is hindered by the extra substitution on the attacking radical. Furthermore, the absence of any detectable uncyclized products prevents extraction of absolute rate data from the product ratios. Lastly, the necessary auxiliary kinetic data are unavailable to convert the product ratios into rates. All that can be concluded is that, as the temperature is increased, the decrease in the 5-exo/6-endo ratio suggests a change from kinetic to thermodynamic control.

In a computational approach to the diamond CVD process, Shokov et al.[9] calculated, among other things, the relative enthalpies for the three radicals **1**−**3** and the transition states by which they interconvert (in their "small" cluster calculations). The computed results for the three radicals, listed in Table 3, provide the connection to experimentally accessible kinetics that can justify (or not) the choice of computational method applied to the larger clusters that were used in that study to model the diamond [100] surface.

Because of the size of the computational problem, the surface radical structures were treated with the PM3 semiempirical Hamiltonian at the unrestricted Hartree−Fock (UHF) level. The primary motivation of the present

(10) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley Interscience: New York, 1992; p 752.
(11) Chuang, C. P.; Gallucci, J. C.; Hart, D. J.; Hoffman, C. *J. Org. Chem.* **1988**, *53*, 3218.

(12) Yurchenko, A. G. In *Cage Hydrocarbons*; Olah, G. A., Ed.; Wiley: New York, 1990; Chapter 5.
(13) Yurchenko, A. G.; Zosim, L. A.; Dovgan, N. L.; Verpovsky, N. S. *Tetrahedron Lett.* **1976**, 4843. Yurchenko, A. G.; Zosim, L. A.; Dovgan, N. L. *Zh. Org. Khim.* **1974**, *10*, 1996.

study is to check these computational results against a model system for which experimental data can be obtained. As noted in ref 9, the kinetics of the surface rearrangements are not rate-limiting in the existing CVD process at 1200 K. Nevertheless, any attempt to run the reactions for CVD, or an analogous set of reactions, at lower temperatures would eventually run into a kinetic bottleneck imposed by the radical reactions investigated here. We therefore judged it important to obtain reliable, quantitative experimental data on the reactions of **1**–**3**.

The product ratios in Table 1 can be converted to absolute rates with the aid of some auxiliary kinetic information. As mentioned in the results section, generation of **2** gave only **5**, while generation of **3** gave only **6**. Only **1** gave all three trapping products. Moreover, the temperature dependence of the trapping product ratios from **1** over the 75–126 °C range, where we trust the data, manifests itself primarily in the reduction in the amount of **4** to a level below that which we can reliably make an absolute determination. The ratio of **5** to **6** appears to change very slowly. An Arrhenius plot with such data would not produce credible results. Instead, the data from the runs at 75 °C, which after all, were repeated many more times than the higher temperature runs and were also subject to fewer possible systematic errors, can be converted to rates for the reactions **1** → **2** and **1** → **3** by using previously reported kinetic data for the chlorine abstraction reactions by primary, secondary, and tertiary radicals from CCl_4. The reactions of *n*-butyl, cyclopentyl, and *tert*-butyl radicals with CCl_4 have been determined by time-dependent ESR spectroscopy.[14] We use the Arrhenius parameters from that report to compute the rates for chlorine abstraction by **1**–**3**, which must occur in kinetic competition with isomerization of the radicals. Several other investigations[15] report kinetic data for either only one of the three classes of alkyl radicals or report rates only at a single temperature. An examination of the different determinations finds that no significant differences in the derived activation energies for the **1** → **2** and **1** → **3** reactions would occur if auxiliary data from one of the other reports were to have been used. We used the kinetic parameters from ref 14 primarily so that the final kinetic simulations could be done with a consistent set of trapping rates.

Taking the density of CCl_4 at 75 °C ($\rho = 1.4864$),[16] the neat solvent is 9.66 M. The pseudo-first-order rate constants for chlorine abstraction from CCl_4 by primary, secondary, and tertiary radicals are then, $k_{1°} = 1.81 \times 10^6$, $k_{2°} = 1.62 \times 10^5$, and $k_{3°} = 8.52 \times 10^5$ s^{-1}. Using the trapping rate, $k_{2°}$, as a clock, the first-order rate constants for the reactions **1** → **2** and **1** → **3** are, therefore, $k_{1→2} = 9.2 \times 10^6$ and $k_{1→3} = 1.7 \times 10^5$ s^{-1} at 75 °C. Using the Arrhenius pre-exponential factor for the parent 5-hexenyl rearrangement,[17] log $A = 10.37 \pm 0.32$, the activation energies for the radical isomerizations become $E_a[\mathbf{1} \to \mathbf{2}] = 5.4 \pm 1.0$ and $E_a[\mathbf{1} \to \mathbf{3}] = 8.2 \pm 1.0$ kcal/mol. The

error boundaries due to propagation of the experimental uncertainty in the product ratios are much smaller than the reported error boundaries reported for the absolute chlorine abstraction rates, so the latter are almost entirely responsible for the ± 1.0 kcal/mol boundaries on the two derived activation energies. A potential source of a systematic error would be the underestimation of the Arrhenius preexponential factor for the more rigid system in the present study. For each factor of 10 increase in A, one would need to increase the derived E_a by 1.6 kcal/mol.[18]

To complete the potential surface for the interconversions of **1**–**3**, we need the relative enthalpies for the three radicals themselves. Combined with the activation energies derived above, the enthalpies would give the activation energies for the reverse processes. The enthalpy of formation for the 1-adamantyl radical has been experimentally determined[19] to be $\Delta H_{f,298}[\mathbf{3}] = 14.8 \pm 2.0$ kcal/mol, but for neither **1** nor **2** are there experimental data. Nevertheless, values for $\Delta H_{f,298}[\mathbf{1}]$ and $\Delta H_{f,298}[\mathbf{2}]$ should be obtainable with high reliability by combining a molecular mechanics calculation for the corresponding hydrocarbon with canonical primary, secondary, and tertiary bond dissociation energies. Polycyclic hydrocarbons like 3-methylenebicyclo[3.3.1]nonane and 3-methylnoradamantane are precisely the kind of structures for which empirical force fields are parameterized. Test calculations on 13 bicyclic, tricyclic, and tetracyclic hydrocarbons[20] with the MMX force field produces heats of formation with a root mean square (rms) deviation from experiment of less than 1.0 kcal/mol. The molecular mechanics calculation gives $\Delta H_{f,298}$[methylenebicyclononane] $= -11.7$ kcal/mol and $\Delta H_{f,298}$[methylnoradamantane] $= -23.2$ kcal/mol. Combining these with critically-evaluated C–H bond energies[21] produces $\Delta H_{f,298}[\mathbf{1}] = 34.8 \pm 1.1$ and $\Delta H_{f,298}[\mathbf{2}] = 25.8 \pm 1.1$ kcal/mol. As a control, the heat of formation of the 1-adamantyl radical, computed in the same manner, is $\Delta H_{f,298}[\mathbf{3}] = 12.9 \pm 1.1$ kcal/mol, which compares well with the number from experiment. The results for the three radicals and the two transition states are listed in Table 3. A check of the final results can be made by performing a kinetic simulation of the rearrangement and trapping reaction sequence using PowerSim, a program for modeling nonlinear dynamics with feedback, like chemical kinetics. The activation parameters from Table 3 are input with those for chlorine abstraction and run at the four temperatures listed in Table 1. The resulting product ratios are listed in parentheses in Table 1. The good agreement within the uncertainty boundaries indicates that the derived activation parameters realistically model the observed chemistry.

Comparison of the calculated thermochemistry with

(14) Hawari, J. A.; Davis, S.; Engel, P. S.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 4721.

(15) Giese, B.; Hartung, J. *Chem. Ber.* **1992**, *125*, 1777. Katz, M. G.; Horowitz, A.; Rajbenbach, L. A. *Int. J. Chem. Kin.* **1975**, *7*, 183. Fritz, P. G.; McLauchlan, K. A. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 87. Johnston, L. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1986**, *108*, 2343.

(16) The density of carbon tetrachloride over a range of temperatures is tabulated by: Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1950.

(17) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

(18) In the final POWERSIM calculation of the product ratios, listed in Table 1 as the numbers in parentheses, indistinguishable product ratios can be obtained for a 100-fold higher A factor if the activation energies are correspondingly reduced by 3.2 kcal/mol. Nevertheless, given that log A < 13 is a safe assumption, the systematic error is not too large. A redetermination of absolute rate constants for Cl-abstraction by adamantyl radical is also in progress to check the assumptions.

(19) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162.

(20) The 13 hydrocarbons are the test set for polycyclic systems in: Engler, E. M.; Andose, J. D.; v. Schleyer, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 8005. The prediction of reliable heats of formation by empirical force fields is validated in this paper.

(21) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

the numbers reported here finds that the qualitative behavior of the system is well-modeled by the relatively modest level of theory used by Shokov et al.[9] By extension, the larger-scale computations for the diamond [100] surface are likely to be qualitatively correct. Nevertheless, the deviations are still large enough that the actual rates and equilibrium constants would be substantially different from the predicted values. For the present high-temperature CVD process, e.g., in a filament-assisted CVD reactor, the deviations may in fact be inconsequential because of the rate-limiting mass transport to the surface, but for any potential low-temperature analog of CVD, the rates become important. The most significant finding in this regard is that the activation barriers for the interconversions between surface radical structures are even lower than predicted by theory. If a functional substitute for H$\cdot$ and $\cdot$CH$_3$ in the CVD process could be designed, the only step that would require even moderately high temperatures would be the desorption of H$_2$ in the 2×1 reconstruction of the [100] surface. All of the other reactions would be efficient at temperatures many hundreds of degrees below the 1200 K surface temperature in present CVD reactors. Curiously, ab initio calculations at the MP2/6-31G* level of theory, shown in Table 3—again, a relatively low level that could be used for larger clusters modeling a surface—do a rather poor job of reproducing the energetics for the isomerization. One concludes that the semiempirical approach by Shokov et al.[9] is a good compromise between numerical accuracy and computational expense.

Conclusions

Model radical systems for the surface radicals in the chemical vapor deposition of diamond are prepared and trapped. Product ratios are used to derive absolute rates for the isomerizations predicted to be important in the incorporation of added carbon atoms into the diamond lattice. The results from the small model systems agree qualitatively with calculations at the relatively low level of theory that are used for the computation of a large section of the diamond surface. We find that the principal difference from the calculated results is the overestimation of activation energies by the calculation.

Experimental Section

Radicals **1**–**3** were prepared by the pyrolysis of the Barton precursors[22] derived from the corresponding alcohols, oxalyl chloride, and the sodium salt of thiopyridine *N*-oxide. This approach was chosen from among several other prospective routes because of the synthetic availability of the three alcohols, convenience in radical generation, and clean subsequent radical chemistry. The latter condition is critical for any quantitative determinations.

In the preparative work, ^{1}H NMR spectra were recorded on a Varian GEMINI 200 MHz spectrometer. Chemical shifts are reported in ppm relative to TMS. Analysis by GC/MS was done with a Fisons GC8060/MD800 instrument fitted with a DB-5ms capillary column. In a typical run, the column temperature was ramped from 50 to 108 °C over 4 min, followed by a subsequent ramp up to 220 °C over 22 min. Quantitative determinations by GC/MS were done relative to anthracene as a standard. Response factors were determined by independent synthesis of the trapping products and co-injection of known amounts of the products with anthracene.

Chloroadamantane was obtained from Aldrich Chem. Co. FT-IR spectra were recorded on NaCl plates with a Perkin-Elmer Paragon 1000. Melting points are uncorrected.

1,3-Dibromoadamantane. Bromination of adamantane followed the procedure by Baugham.[23] Br$_2$ (216 mL, 4.12 mol), BBr$_3$ (7.8 mL, 82.0 mmol), and Al$_2$Br$_6$ (1.0 g) were placed in a 1 L three-necked flask fitted with a mechanical stirrer and tubing leading to two gas washbottles (filled with concd Na$_2$S$_2$O$_5$ solution) and placed in an ice bath. Adamantane (50 g, 367 mmol, Aldrich Chemical Co.) was added slowly. After addition was complete, the ice bath was removed. After 30 min, gas evolution ceased, and the reaction mixture was heated to reflux for 3 h. The reaction mixture was then cooled again in an ice bath and quenched with a concd solution of Na$_2$S$_2$O$_5$, resulting in vigorous evolution of both gas and heat. Further Na$_2$S$_2$O$_5$ was added as a solid until the reaction mixture changed color. After neutralization with NaHCO$_3$, the mixture was filtered and extracted with chloroform. The combined organic fractions were dried over sodium sulfate, redissolved in ether, washed with further concd Na$_2$S$_2$O$_5$, dried over magnesium sulfate, and evaporated under reduced pressure, yielding 87.5 g (81%) of crude 1,3-dibromoadamantane. An aliquot for analysis was recrystallized from methanol: mp 112 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.70 (br, 2H), 2.29 (br, 10H), 2.88 (s, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 33.5, 34.1, 46.4, 58.7, 62.0.

3-Methylenebicyclo[3.3.1]nonan-7-one. The procedure from Gaugneux was followed.[24] Dibromoadamantane (30 g, 102 mmol) and 300 mL of 1 N aqueous NaOH were placed in a steel autoclave filled with 270 mL of dioxane. The autoclave was brought to 180 °C over 2 h and maintained at that temperature for an additional 30 min. The reaction mixture was washed with aqueous NH$_4$Cl, extracted with chloroform, and dried over sodium sulfate. Recrystallization from methanol yielded 9.2 g (60%) of the product, which sublimes at 158–161 °C (sealed tube): ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.92 (br, 2H), 2.20–2.50 (br, 10H), 4.78 (s, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 30, 32, 41, 47, 114, 141, 211.

3-Methylenebicyclo[3.3.1]nonan-7-ol.[25] Reduction of methylenebicyclononanone (1.76 g, 12 mmol) with LiAlH$_4$ (0.22 g, 5.6 mmol) proceeded by slow, dropwise addition under dry N$_2$ of the ketone dissolved in 10 mL of THF into a stirred suspension of the hydride suspended in 15 mL of THF. After 1 h at reflux and 4 h at rt, a concentrated solution of sodium sulfate was added dropwise until a precipitate formed. The reaction mixture was then diluted with THF, filtered, and dried over sodium sulfate and the solvent evaporated to yield 1.5 g (86%) of a white solid. The 3:1 mixture of endo vs exo alcohol was separated by flash chromatography over silica using hexane/EtOAc in a 5:1 ratio. Endo isomer: mp 82–3 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.53–1.68 (m, 4H), 2.10–2.49 (br, 8H), 2.99 (d, J = 12 Hz, 1H), 3.78 (m, 1H), 4.90 (m, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 28.16, 32.41, 39.83, 39.74, 62.93, 112.10, 148.35. Exo isomer: mp 86–7 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.16 (s, 1H), 1.44 (td, 2H), 1.59 (m, 2H), 2.01 (br, 2H), 2.18 (t, 2H), 2.33 (br, 4H), 4.58 (m, 1H), 4.63 (m, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 28.34, 31.23, 37.64, 39.64, 61.83, 106.59, 146.45.

3-Noradamantylmethanol. BH$_3$·THF (1 M, 9.7 mL, 9.7 mmol) was added dropwise to a stirred solution of the commercially available noradamantanecarboxylic acid (1.01 g, 6.1 mmol) in 10 mL of THF and stirred at rt overnight. The solution was then quenched with water and extracted with ether. The organic washes were dried and then evaporated to yield 0.91 g of a white solid (98%): mp 146 °C (lit.[26] 142–4 °C); ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.4 (br, 10H), 2.10 (br, 1H), 2.24 (br, 2H), 3.63 (s, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 35.23, 37.15, 40.28, 43.71, 45.62, 50.73, 68.83.

Radicals 1–3: Atmospheric Pressure Procedure. The

(22) Barton, D. H. R.; Crich, D. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1603.

(23) Baugham, G. L. *J. Org. Chem.* **1964**, *29*, 238.
(24) Gaugneux, A. R.; Meier, R. *Tetrahedron Lett.* **1969**, 1365.
(25) Stehelin, L.; Kanellias, L.; Ourisson, G. *J. Org. Chem.* **1973**, *38*, 851.
(26) Vogt, B. R.; Hoover, J. R. E. *Tetrahedron Lett.* **1967**, *30*, 2841.

3-methylenebicyclo[3.3.1]nonan-7-yl radical (**1**), (3-noradamantyl)methyl radical (**2**), and 1-adamantyl radical (**3**) were prepared according to two procedures. For the runs at 75 °C, i.e., refluxing CCl$_4$ at atmospheric pressure, the procedure for **1** is given here as representative. The radicals were formed from the alcohol by the Barton thiohydroxamate route.[22] A solution of 0.045 g (0.29 mmol) of the *exo*-3-methylenebicyclo[3.3.1]nonan-7-ol in 10 mL of benzene was added dropwise via cannula over 30 min to a solution of 0.88 mL (1.75 mmol) of oxalyl chloride in 10 mL of benzene under inert gas. After the addition was complete, solvent and excess oxalyl chloride were removed by evaporation under a stream of dry N$_2$. The mixture was redissolved in 5 mL of benzene. An aliquot was removed, filtered through a plug of silica gel, and analyzed by GC/MS to determine the amount of "premature" chloroadamantane. The remainder of the solution was added dropwise with vigorous stirring to 150 mL refluxing CCl$_4$ containing an equimolar amount of suspended thiopyridine *N*-oxide sodium salt. Within the first 2 min of the 10 min addition, the solution turned yellow but became white again after a further 15 min. An aliquot was then removed, filtered through silica gel, and analyzed by GC/MS. The remaining solution was carefully evaporated, redissolved in CDCl$_3$, and analyzed by NMR.

Radicals 1–3: High-Pressure Procedure. Higher temperature runs were performed in a sealed, thermostatically-controlled high-pressure bomb reactor. Again, a representative procedure for **1** is described. Preparation of the oxalate ester of *exo*-3-methylenebicyclo[3.3.1]nonan-7-ol proceeded as noted above. An aliquot was removed prior to further reaction to assay "premature" chloroadamantane. The bomb reactor was fitted with a pressure-equalizing addition vessel with stainless steel valves, pressure sensor, a temperature controller with a thermistor sensor in contact with the solution, and a belt-driven mechanical stirrer. The bomb was charged with 150 mL of CCl$_4$ and an equimolar amount of the thiopyridine *N*-oxide sodium salt and stirred vigorously for 3 h to achieve uniform suspension of the solid. The bomb was further pressurized and purged with 20 atm of N$_2$ three times in succession to check for leaks and remove traces of oxygen. After the purging, the bomb was brought to the desired internal temperature. The adduct of the alcohol and oxalyl chloride in the addition vessel was added in small "squirts" every 60 s over a period of 30 min with vigorous stirring in the bomb. After the addition was complete, the addition vessel was briefly pressurized and residual solution flushed into the reactor. The bomb was held at the desired temperature for 15 min and then quenched to room temperature. The reaction mixture was then analyzed as described previously.

3-Methylene-7-chlorobicyclo[3.3.1]nonane (4). *endo*-3-Methylenebicyclo[3.3.1]nonan-7-ol (1.0 g, 6.57 mmol) was dissolved in pyridine to which 1.38 g (7.23 mmol) of *p*-toluenesulfonic acid chloride was added. After the mixture was stirred overnight, 0.56 g of lithium chloride (13.14 mmol) was added, and after 24 h, the reaction mixture was extracted with pentane, the extracts were washed with dilute acetic acid and water and dried over MgSO$_4$, and the solvents were removed to yield 1.59 g of a colorless oil that was purified by column chromatography on silica gel (hexane). A 2:5 mixture of 1-chloroadamantane and 3-methylene-7-chlorobicyclo[3.3.1]nonane (**4**) was obtained and separated by HPLC (RP-18 column, MeOH, 30% H$_2$O). The HPLC fractions were quickly exracted with pentane to avoid product decomposition, the fractions containing the desired product were combined and dried (MgSO$_4$), and the solvent was removed carefully to avoid loss of the volatile compound. After sublimation, 0.038 g of **4** was obtained (3.4%): mp 61 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.68 (br, 2H), 1.87 (td, 2H), 2.13–2.32 (br, 4H), 2.39 (br, 4H), 4.71 (m, 2H), 4.92 (m, 1H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 29.39, 30.85, 37.29, 41.10, 52.88, 107.19, 146.14; GC/MS (DB-5 ms, 70 eV EI) 14.6 min, m/e = 170 (M$^+$, 10), 92 (100), 78 (95); HRMS for C$_{10}$H$_{15}$Cl (M$^+$) calcd 170.0857, found 170.0856.

3-Noradamantylchloromethane (5). 3-Noradamantylmethanol (120 mg, 0.79 mmol) was dissolved in 5 mL of benzene and added dropwise to a 2 M solution of oxalyl chloride in dichloromethane (2.4 mL, 4.8 mmol) that had been further diluted with 5 mL of benzene. After stirring, the solvents and excess reagents were removed by a stream of dry N$_2$. The residue was redissolved in 5 mL of benzene and added dropwise to a suspension of the thiopyridine *N*-oxide sodium salt (302 mg, 2.0 mmol) in 200 mL of carbon tetrachloride over a period of 3 h. The reaction mixture was then filtered, and the majority of the solvent was distilled off. The concentrated solution was eluted through a silica gel column with pentane. The solvent was carefully removed by distillation to yield 23 mg (17.1%) of **5** as a colorless oil: ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.50−1.80 (br, 10H), 2.11−2.30 (br, 3H), 3.63 (s, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 34.76, 37.20, 41.74, 43.46, 46.66, 50.34, 52.53; GC/MS (DB-5 ms, 70 eV EI) 13.1 min, m/e = 170 (M$^+$, 7), 135 (60), 79 (100); HRMS for C$_{10}$H$_{15}$Cl (M$^+$) calcd 170.0857, found 170.0852.

Computational Details. Heats of formation for (nonradical) hydrocarbons that are unavailable by calorimetry were determined by molecular mechanics using the MMX force field derived from MM2 in the PCModel program (Serena Software) on an IBM-compatible PC. The calculated heats of formation for a number of cage and bicyclic compounds closely match experimental values for those cases when the data exist for the comparison. For example, the lowest energy conformer of [3.3.1]bicyclononane is computed to have ΔH_f = −30.5 kcal/mol, compared to −30.49 kcal/mol by experiment.[27] Further computations for the isomerizations **1** → **2** and **1** → **3** were done at the MP2/6-31G*//PM3 level of theory with the geometries fully relaxed along the reaction coordinate using the Gaussian 92 package of programs[28] running on an IBM RS/6000-590 UNIX workstation. Kinetic simulations were run with PowerSim V2.01 (ModelData AS) on an IBM-compatible PC.

(27) Parker, W.; Steele, W. V.; Watt, I. *J. Chem. Thermodyn.* **1977**, *9*, 307.

(28) Gaussian 92, Revision A, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Resplogle, E. S.; Gomperst, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.