Nanodiamonds

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Synthesis of Higher Diamondoids and Implications for Their Formation in Petroleum**

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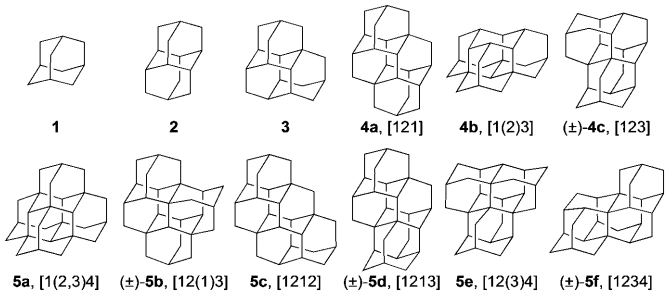
Diamondoids can be thought of as the smallest (ca. 0.5–2 nm, i.e., nanodiamonds) form of hydrogen-terminated cubic diamond. Only the lower members of this series, which starts with adamantane (**1**, Scheme 1),[1] diamantane (**2**),[2]



Scheme 1. The family of diamondoids: lower diamondoids **1**–**3**, the three isomers of tetramantane (**4**), and the six pentamantanes (**5**). The numbers in brackets refer to the unique Balaban–Schleyer nomenclature.[13]

triamantane (**3**)[3] and so forth, can be prepared by chemical synthesis.[4] Of the higher diamondoids, i.e., those that have isomeric forms, only C_{2h}-symmetric [121]tetramantane (**4a**) has been prepared in the laboratory in very low yields.[5,6] All other higher diamondoids are only accessible from raw petroleum.[7] There are three tetramantanes (**4a**[8] and [1(2)3]tetramantane, C_{3v}-**4b**[9]) including one enantiomeric pair (*P*)-(+)- and (*M*)-(−)-[123]tetramantane (**4c**),[10] six pentamantanes (with [1(2,3)4]pentamantane being the first exhibiting a diamond {111} surface[11]), 24 hexamantanes (**6**),[9,12] nearly one hundred heptamantanes (**7**), and so forth.[13] Thus far, diamondoids with up to 11 cages have been shown to exist in petroleum,[7] but no other source is known, although recent studies suggest possible interstellar occurrence.[14] The larger nanodiamonds occur as rigid rods (**4a**, **5c**),[8] discs (**4b**),[9,12] pyramids (**5a**),[11] and helices (**4c**, **5f**),[10] exhibiting quantum confinement[15] and negative electron affinity.[16] They can be specifically derivatized,[8,11,17,18] with electron emission properties superior to any other material[16] making them attractive for molecular electronics.[19]

The mechanism for formation of these nanodiamonds for a long time was attributed to thermodynamically controlled carbocation rearrangements.[20,21] Such mechanisms enable the practical synthesis of **1**–**3** but they fail in the production of the higher diamondoids.[6,21,22] A detailed analysis of the mechanism for adamantane formation from a single starting material shows an amazing 2897 pathways;[23] a more limited analysis of triamantane formation through carbocation pathways indicates at least 300000 potential intermediates.[24] Prospects for higher diamondoid syntheses by these pathways are bleak due to a lack of large polycyclic precursors, problems with intermediates trapped in local energy minima, disproportionation reactions leading to side products, and the exploding numbers of isomers as the size of target higher diamondoid products increases. With the failure of syntheses of higher diamondoids through carbocation rearrangements, attempts at their preparation were abandoned in the 1980s.

Since higher diamondoids occur in relatively high concentrations in petroleum that has undergone thermal cracking (i.e., been subjected to very high temperatures due to deep burial), we began to consider that these free-radical cracking reactions might be involved in higher diamondoid formation. The uncatalyzed formation of **1** and **2** from *n*-alkanes under conditions of cracking was shown recently,[25] presenting evidence that exclusively thermal pathways involving free radicals can readily compete with the typically assumed acid-catalyzed carbocation rearrangements. Such mechanistic proposals underline the notion that diamondoids are thermodynamically the most stable hydrocarbons, i.e., they are more stable than nanographenes (extended polycyclic aromatic hydrocarbons)[26] of comparable molecular weight.[27] Moreover, the relative stabilities of carbocations and alkyl radicals

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are quite different, especially when polycyclic structures are taken into account. For instance, while the secondary and tertiary diamondoid C–H bonds have practically the same bond dissociation energies,[28] the heterolytic cleavages of these bonds differ significantly in energy.[29] As the isomer distribution in the extracts from raw oil does not reflect the thermodynamic stability of the diamondoids or their cations,[7,18] a different formation mechanism must be considered. Here we present firm evidence for a radical mechanism that leads to the first direct synthesis of higher diamondoids from lower diamondoids. This has implications for diamond formation and diamond surface reconstruction.

In an attempt to test the thermal cracking hypothesis for the formation of higher diamondoids, we performed a series of sealed tube pyrolysis experiments under conditions that simulate natural oil cracking.[30] We were particularly interested in whether lower diamondoids may serve as precursors for higher diamondoids. Therefore, we began with pyrolyzing a sample of **3** in an evacuated sealed gold tube at 500 °C for 4 d in order to crack some, but not all of **3**, with the idea in mind that free alkyl radicals would be generated that could react with the remaining intact triamantane molecules or radicals. Remarkably, although the main diamondoid products of these experiments are alkylated triamantanes, all tetramantane isomers (**4**) form, although the yields are small (on the order of thousands of ppms); very small amounts of the pentamantanes (**5**) also form (Table 1).

In addition to the triamantane heating experiments, we conducted cracking experiments with each of the three tetramantanes (**4a**–**4c**) to determine if any of the six pentamantanes could be synthesized: Pentamantanes were in fact generated (Table 1, B–D). Those formed by the replacement of three tetramantane hydrogens with carbons to form a new cage without breaking any of the original tetramantane bonds, are highly favored (Figure 1). The most preferred are those with the least steric crowding. Where the breaking of a tetramantane cage is required to form a particular pentamantane, that pentamantane is either generated in very small relative amounts or not at all. For instance, there are only three ways of adding an additional isobutane unit (i.e., another adamantyl moiety) to an existing diamondoid face of [121]tetramantane (**4a**) without changing the [121] core structure: This results in [12(1)3] (**5b**), [1212] (**5c**), and [1213] pentamantane (**5d**). The remaining three pentamantanes **5a**, **5e**, and **5f** do not form as this would require breaking and reconstructing the cage. This implies that the starting diamondoid cage is retained in the growth process and all bond breaking–bond making events involve only surface hydrogens, akin to CVD growth.[31]

As a measure of the relative steric hindrance encountered for the various isomers, Table 1 also lists the number of 1,3-diaxial interactions on the reactant faces for the formation of a specific pentamantane isomer. The greater the number of these interactions, the less likely the formation of this isomer.

As each cage closure necessary to make the next larger diamondoid formally requires an isobutyl moiety, isobutane and isobutene were added to the starting diamondoid and another set of heating experiments was conducted. These conditions are akin to those of gas condensates where diamondoids form under high pressure and high temperatures.[7] Table 1 shows that the yields of higher diamondoids can be greatly increased, in many cases by roughly an order of magnitude. It is not known whether this improvement is due to the propensity of the branched isobutane or isobutene to crack and form free radicals that add one carbon at a time or whether isobutyl radicals add directly to diamondoid radicals to form the next larger diamondoid through dehydrogenations and ring-closures.

Table 1: Formation of higher diamondoids from triamantane (**3**, part A) and all three tetramantanes (**4**, parts B–D) through cracking at 500 °C in a sealed gold tube (for 4 d), without and with isobutane or isobutene added.[a]

A			
Reactant→ Product↓	**3**	**3** + Isobutane	**3** + Isobutene
[1(2)3]Tetramantane (**4b**)	1567 (1041)	11413 (11333)	16274 (27300)
[121]Tetramantane (**4a**)	718 (402)	7163 (7482)	8576 (14832)
[123]Tetramantane (**4c**)	183 (93)	1304 (1669)	1782 (3890)
[1(2,3)4]Pentamantane (**5a**)	2	183 (226)	141 (319)
[12(1)3]Pentamantane (**5b**)	13	299 (429)	229 (658)
[1212]Pentamantane (**5c**)	5	182 (292)	137 (411)
[1213]Pentamantane (**5d**)	6	125 (185)	92 (288)
[12(3)4]Pentamantane (**5e**)	0.9	8 (13)	9 (20)
[1234]Pentamantane (**5f**)	0.4	–	–

B, [121]Tetramantane (**4a**)				
Reactant→ Product↓	1,3-Diaxial interactions[b]	**4a**	**4a** + Isobutane	**4a** + Isobutene
5b	6	104	2922	1005
5c	3	114	7637	1970
5d	6	34	2634	617

C, [1(2)3]Tetramantane (**4b**)				
Reactant→ Product↓	1,3-Diaxial interactions[b]	**4b/8**	**4b** + Isobutane	**4b** + Isobutene
5a	3	1723	2995	1341
5b	6	332	2552	872
5c	–[c]	–	62	21
5d	–[c]	–	79	6
5e	12	–	62	11

D, [123]Tetramantane (**4c**)				
Reactant→ Product↓	1,3-Diaxial interactions[b]	**4c**	**4c** + Isobutane	**4c** + Isobutene
5a	–[c]	–	–	–
5b	3	497	5886	1116
5c	–[c]	214	231	37
5d	3	41	3318	613
5e	5	39	462	60
5f	5		638	97

[a] Yields are given in ppm from GC/MS analysis with authentic internal standards of all diamondoids. Numbers in parentheses are second runs of the same experiment. [b] On the reactant face, with respect to product isomer formed. [c] "–" Indicates that this product cannot form directly from the diamondoid precursor.

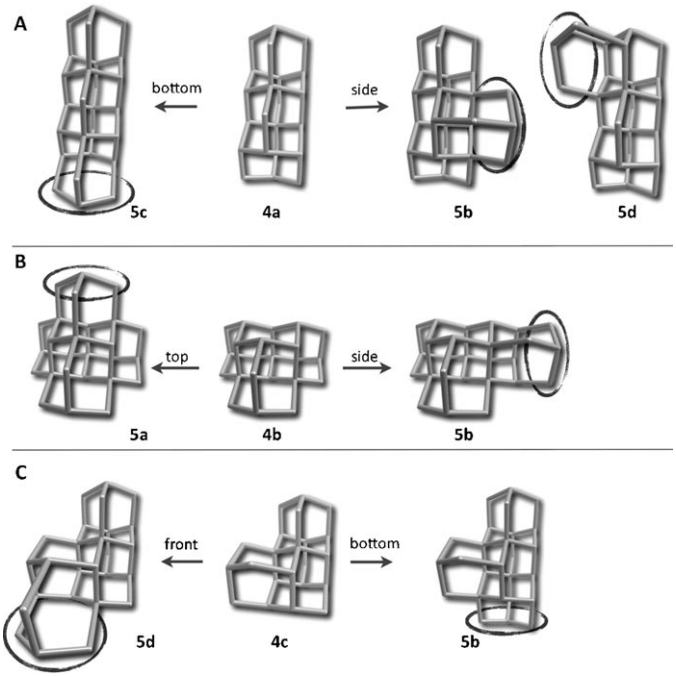

Figure 1. Preferred growth products of diamondoids **4a**–**4c** under preservation of the original diamondoid core structure. The added isobutyl units forming the next higher diamondoid are encircled. Hydrogens omitted for clarity.

To make pentamantanes from the frustum-shaped [1(2)3]tetramantane (**4b**) by the addition of four carbons, it is possible to place an isobutyl group at the top to complete the pyramidal structure of [1(2,3)4]pentamantane (**5a**, Figure 1B). Additionally, by completing cages along the sides of this tetramantane one can make [12(1)3]pentamantane (**5b**, Figure 1B). However, the number of unfavorable 1,3-diaxial interactions (Table 1C) suggests that it will be quite difficult to form [12(3)4]pentamantane (**5e**).[32] As a consequence, the only detectable pentamantanes made by experimental pyrolysis of [1(2)3]tetramantane (**4b**) alone are in fact [1(2,3)4] (**5a**) and [12(1)3]pentamantane (**5b**). Addition of a new cage to form **5a** would have the least steric hindrance (Table 1) and indeed it is the predominant product. When adding isobutane or isobutene to the starting tetramantane, upon heating this results in formation of relatively small amounts of the other pentamantanes including **5e**, along with **5c**, and **5d**, apparently formed by a minor, possibly alternative mechanism.

Lastly, by adding an isobutyl group to [123]tetramantane (**4c**), one could theoretically make [1234] (**5f**), [12(3)4] (**5e**), [1213] (**5d**), or [12(l)3]pentamantane (**5b**) (Figure 1C); steric considerations would favor the formation of **5b**. Experimental data in Table 1 for heating **4c** alone show that all of these pentamantanes in fact form, with the exception of **5f**, with **5b** predominating. As expected, no detectable **5a** or **5c** formed.

It is evident from these experiments that diamondoids are being "built up" by the addition of four carbons replacing three hydrogens on the starting diamondoid to complete a cage thus forming the next larger diamondoid in the series. This mechanism seems analogous to diamond growth in a CVD chamber, which involves a reducing atmosphere consisting of over 90% hydrogen, much of it in atomic form to keep the diamond surface hydrogen passivated.[33] Diamond growth is derived from the addition of methyl and/or larger radicals replacing hydrogen on the surface of small diamond seeds that are necessary for initiation of the process. In this way, new cages form and the size of the diamond increases. This process takes place at temperatures generally in excess of 450°C; pressures are usually near atmospheric.[31] Conditions are less optimal for CVD diamondoid growth in natural gas (predominantly methane) fields, with temperatures generally not exceeding 200°C, and undoubtedly, the supply of methyl and other radicals must be very low. However, the geological time frames are considerable, with oil generation and oil cracking taking place over millions of years.

In order to test the CVD hypothesis, we grew microcrystalline diamond in a CVD reactor using the largest diamondoid currently available, [121321]heptamantane (**7a**) as seeds. Figure 2 is a scanning electron micrograph (SEM) of microcrystalline diamond produced by CVD nucleated using **4** as the higher diamondoids. The analysis of the SEM pictures implies a high nucleation density as a result of rubbing with diamondoids that is different from simple hydrocarbons and other ways of preparing surfaces for CVD diamond growth. Diamondoids apparently strongly bond to the surface by tribological action including (local) high temperature and mechanical force spikes; there was no nucleation when diamondoids were simply left on the surface without applying mechanical stress. That

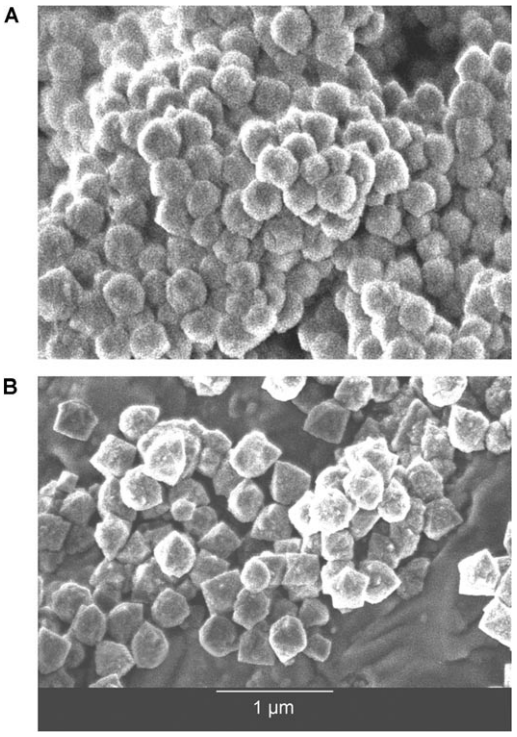

Figure 2. Scanning electron micrograph (SEM) of diamond produced by chemical vapor deposition (CVD) using A) Russian detonation nanodiamond and B) [121321]heptamantane (**7a**) as seed crystals under otherwise identical experimental conditions.

is, diamondoids show the behavior of small particles despite their tiny size, and they offer an interesting chemical-mechanical compromise to nucleating diamond that leaves the substrate surface essentially intact compared to existing technologies. This unique feature may be exploited for diamond heteroepitaxy that requires undamaged substrate diamond interfaces.

Based on the studies presented here, it seems plausible that, on the way to microcrystalline diamond, tetramantanes grew through the addition of carbon radicals to become pentamantanes, then hexamantanes, etc. until a diamond crystal of micron size emerged. It seems that if this free-radical mediated progression could be curtailed, production of higher diamondoids would be possible.

This is the first proposal of a CVD-type diamond growth mechanism in oil and gas fields. It could well be that larger diamondoids or even diamonds exist within the reservoir, but are not soluble in the migrating fluids, oil, and gas. Microcrystalline diamonds could be the product of the growth processes suggested here, and, being too large to be soluble in migrating petroleum or gas, would remain in the petroleum reservoir. Intriguingly, microcrystalline black diamonds (carbonados), are believed to be formed in the Earth's crust.[34] The origin of carbonados has remained uncertain based on mineralogical data and unusual $^{12}C/^{13}C$ isotopic ratios that are similar to petroleum rather than mantle-derived carbon.[35]

Higher diamondoids form from lower ones in experiments mimicking petroleum cracking. The yields are low but can be significantly improved by the addition of isobutane or isobutene. Rather than through superacid-catalyzed carbocation rearrangement reactions—long assumed to be responsible for diamondoid growth—our experiments take place through free-radical mechanisms that are akin to CVD growth giving microcrystalline diamond: Higher diamondoids can be used as seeds to grow CVD diamond. This leads to the conclusion that if CVD conditions were optimal it should be possible to effectively synthesize larger nanodiamonds of a desired size range using appropriate smaller diamondoids as seeds. Future experiments will include the use of isobutane and isobutene in the CVD carrier gas.

Experimental Section

Thermolyses: Triamantane (**3**) and the tetramantanes (**4**) were isolated from petroleum by methods described elsewhere.[7] They were re-crystallized eight times from *n*-hexane to remove impurities, which were determined quantitatively by GC-MS (conditions described below) using [D_4]-**2** as internal standard. 25 mg of purified diamondoid were loaded into gold-lined stainless steel pressure vessels. The vessels were then purged with argon and heated for 96 h and 500 °C. After heating, the products were spiked with a known amount of [D_4]-**2** recovered by repeated rinsing with hexane. In the isobutane/isobutene experiments, 0.894 g isobutane (0.412 mg isobutene) were added to 27 mg (24 mg) of **3**, respectively. A diamondoid plus additional hydrocarbon product fraction was obtained by passing 200 μL of the spiked product over an activated silica gel column in 2 mL of *n*-hexane. Diamondoid identification was performed by GC-MS utilizing a HP6890 GC and a VG Autospec Q mass spectrometer, in full-scan mode comparing mass spectra and retention times with authentic standards for each diamondoid for identification. Quantitation was performed by selected ion monitoring of the ions *m*/*z* 175, 187, 188, 192, 201, 239, 240, 244, 253, 291, 292, 305, 330, 342, 344, and 396. We used a DB-1 column, 60 m, 0.25 mm ID, 0.25 μm film thickness. Our temperature program started at 80 °C with a 1 min hold time and then 5 °C min^{-1} to 320 °C with a 30 min hold time. Ionization was by electron impact (EI) at 70 eV and we used hydrogen as a carrier gas.

Nucleation experiments: A single crystal silicon {100} surface was divided into quadrants and prepared by rubbing a cloth impregnated with nano-sized diamond grit (Russian detonation diamond) or diamondoids as described here and then subjected to typical CVD diamond growth conditions using microwave plasma CVD. Deposition conditions: microwave plasma 5 kW, pressure 50 torr, gas flow rate 222 sccm (standard cubic centimeter per minute) H_2, 50 sccm CH_4, length of run 60 min, substrate temperature 500 °C.

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