Reaction yields of diamondoid synthesis by plasmas generated in supercritical xenon

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Diamondoids are sp^3 -hybridized carbon nanomaterials that hold promise for application in biotechnology, medicine, and opto- and nanoelectronics. While difficult or even impossible to realize by conventional organic synthesis methods, the synthesis of larger diamondoids was demonstrated by plasmas generated in supercritical fluids, however, the reaction mechanisms that lead to their formation are not clear. Here, we investigated the synthesis of diamondoids from adamantane and present a simple model that predicts the reaction rates of diamantane, triamantane, and tetramantane. The diamondoids were synthesized by micro dielectric barrier discharges arranged in arrays, generated at frequencies of 7 kHz and applied voltages of 5 – 10 kV_{p-p} in supercritical xenon (pressure 5.56 – 8.22 MPa, temperature 290.0 – 310.2 K). The collected samples were analyzed and quantified by gas chromatography - mass spectrometry measurements. The reaction yields of diamantane increase with increasing precursor density and longer reaction times. Experimental data also suggests a stepwise reaction of higher diamondoids from lower diamondoids, and predicts lower reaction rates for higher diamondoids when compared to lower diamondoids.

Keywords: Diamondoid synthesis, supercritical fluid, plasma, reaction mechanism

1. INTRODUCTION

Diamond molecules - so-called diamondoids - are a series of sp^3 -hybridized molecules whose carbon framework can be superimposed on a diamond lattice [1]. In contrast to nanodiamonds, which can have different size distributions and whose surface terminations often consist of graphitic shells [2], diamondoids possess a well-defined structure and surface terminations that consist of hydrogen atoms.

Diamondoids have been found to possess many advantageous properties (e.g. high thermal and chemical stability), which make them suitable for many different applications such as in pharmaceuticals and medicine [3, 4]. Because of their negative electron affinity, they also hold promise for optoelectronic applications [5,6]. Furthermore, they offer the possibility of bandgap tuning, which can be achieved by changing their size, by the attachment of functional groups [7], or even by the encapsulation of small atoms or ions (e.g. H, Li, Be, Na, Mg etc.) inside their cages [8]. This makes them suitable as possible building blocks for functional nano structures [9] and in contact with metal surfaces, they could also be used in molecular electronics [10].

While higher diamondoids that are composed of more than four units were first isolated from crude oil [11, 12], the availability of diamondoids above the

2nd member, diamantane, is limited. Many attempts have been undertaken to obtain diamondoids synthetically, but with the exception of triamantane [13] and anti-tetramantane [14], no other diamondoids have been obtained by conventional organic synthesis. The reason is that with increasing diamondoid size, the number of possible reaction pathways and reaction intermediates increases exponentially [15], making such approaches impractical or even impossible. Therefore, other, alternative methods are needed to synthesize diamondoids.

Electric discharges generated in supercritical CO₂ [16], supercritical water and xenon [17] have shown a critical anomaly in the breakdown voltage near the critical point, exhibiting a local minimum. Furthermore, such high-density plasmas have shown promise for the synthesis of carbon nanomaterials [18] and the deposition of metallic films [19].

Recently, it has been demonstrated that nanodiamonds [20] and diamondoids can be synthesized both by dielectric barrier discharges (DBDs) [21–23] and pulsed laser ablation plasmas in supercritical xenon (scXe) [24] and CO₂ [25]. In these reports, the diamondoids were characterized by energy-dispersive X-ray spectroscopy, micro-Raman spectroscopy, and gas chromatography - mass spectrometry (GC-MS). While it has been found that synthesis near the critical point of xenon leads to higher reaction yields [22], the

effect of other parameters such as the precursor density and the evolution of the product quantities have not been investigated in detail yet.

Here we present the effect of the amount of the precursor and the reaction times on the synthesis of increasingly larger diamondoids using the first diamondoid, adamantane as a precursor. The advantage of using adamantane is that can be synthesized in large quantities [26] and is therefore cheap, and it is expected to act as a seed to which increasingly larger diamondoid cages can be attached. In addition, we propose a simple reaction model to simulate reaction rates for the synthesis of diamondoids.

2. EXPERIMENTAL APPROACH

The experimental setup and procedure used for generating the DBD plasmas in scXe using arrayed microelectrodes has already been reported in detail before [21, 22]. The electrodes and the diamond precursor adamantane (molecular mass $\sim 136 \text{ g mol}^{-1}$) were placed in a custom-made high-pressure cell. In the present experiments, the gap distance of the electrodes and the thickness of the dielectric were 70 ± 10 and $100 \pm 10 \mu\text{m}$, respectively. The electric discharges were generated by applying a sine wave signal produced by a function generator (WF1946B, nf Corp.) and an AC high-voltage amplifier (HVA4321, nf Corp.).

For the synthesis, the temperature and pressure were maintained at values close to the critical point of Xe (critical temperature $T_{\text{crit}} = 289.75 \text{ K}$, critical pressure $p_{\text{crit}} = 5.84 \text{ MPa}$), in the ranges of $p = 5.56\text{--}8.22 \text{ MPa}$ and $T = 290.0\text{--}310.2 \text{ K}$, which correspond to reduced pressure and temperature values of $p_r = p/p_{\text{crit}} = 0.952\text{--}1.408$ and $T_r = T/T_{\text{crit}} = 1.001\text{--}1.071$, respectively. The plasmas were generated for durations between 60 and 120 min at a frequency of $f = 7.0 \text{ kHz}$, and applied peak-to-peak voltages varied between $5\text{--}10 \text{ kV}_{\text{p-p}}$. Table I summarizes the detailed experimental conditions.

After the synthesis, the pressurized chamber was purged and the gas and synthesized products flown through a collection trap filled with cyclohexane. To increase the concentration of the products, the cyclohexane was first evaporated before adding 1 mL of cyclohexane to redissolve the products.

In these experiments, we especially focussed on the characterization of the samples by GC-MS (GCMS-QP2010 Plus, Shimadzu Corp.), using the same carrier gas and temperature ramp as described previously [22, 24]. The GC-MS measurements were conducted by alternating between the selected ion-monitoring mode (SIM) and scan mode. The target mass-to-charge ratio (m/z) numbers that were monitored in the SIM mode corresponded to the relative molecular masses of diamondoids of up to 600, and the scan mode was operated with an m/z range from 40 to 1000.

Table I. Experimental conditions adopted for the DBD generation in scXe. The temperature and pressure ranges expressed by the reduced values ($T_r = T/T_{\text{crit}}$, $p_r = p/p_{\text{crit}}$) correspond to conditions close to the critical point of Xe ($T_{\text{crit}} = 289.75 \text{ K}$, $p_{\text{crit}} = 5.84 \text{ MPa}$).

Parameters		Values	
Pressure	p	5.56 – 8.22	MPa
	p_r	0.952 – 1.408	
Temperature	T	290.0 – 310.2	K
	T_r	1.001 – 1.071	
Applied voltage	V_{appl}	5 – 10	$\text{kV}_{\text{p-p}}$
Applied frequency	f	7.0	kHz
Adamantane quantity	m	1.0 – 13.4	mg
Plasma generation time	t	60 – 120	min

3. RESULTS AND DISCUSSION

3.1 GC-MS measurements

Figure 1 shows the SIM chromatograms and mass spectra of the synthesized product and a standard sample that contained a mixture of adamantane and diamantane. The sample was synthesized at $p = 5.84 \pm 0.02 \text{ MPa}$, $T = 289.9 \pm 0.1 \text{ K}$, $V_{\text{appl}} = 6.8 \text{ kV}_{\text{p-p}}$, $f = 7 \text{ kHz}$.

The upper curve of Fig. 1(a) shows the SIM chromatograms for m/z 188 of the synthesized sample, while the lower curves are the SIM chromatograms of m/z 136 and 188 of the standard sample. The first peak in the lower curve of Fig. 1(a) at a retention time of $t_{\text{ret}} = 3.8 \text{ min}$ is due to adamantane. In the cases of both the synthesized and standard sample there is a peak at $t_{\text{ret}} = 7.2 \text{ min}$ that can be assigned to diamantane.

The corresponding mass spectra acquired at $t_{\text{ret}} = 7.2 \text{ min}$ of the synthesized product and a standard sample [cf. Fig. 1(b)] both contain a prominent peak (labelled $\text{M}^{+\bullet}$) at m/z 188, which is ascribed to the molecular ion peak of diamantane (relative molecular mass $M_r = 188$). In addition to the appearance of the peak at the same retention time ($t_{\text{ret}} = 7.2 \text{ min}$) and the presence of the molecular ion peak at m/z 188, both mass spectra of Fig. 1(b) have similar fragmentation patterns (smaller differences are attributed to the lower quantity of the synthesized sample when compared to the standard sample). This correspondence between retention times and mass spectra proves the synthesis of diamantane.

3.2 Variation of reaction yields

To establish the influence of the supercritical medium and the plasma on the synthesized products, we first investigated the reaction yields of diamantane. For this, the peak areas of the peaks in the SIM $M_r = 188$ spectra [cf. the inset in Fig. 1(a)] were calculated by numerical integration and compared to those obtained from a calibration curve. Figure 2(a) shows the variation of the SIM 188 peak area at a retention time of $t_{\text{ret}} = 7.2 \text{ min}$ as a function of the mass of the precursor adamantane in the range from 1.0 – 13.4 mg. The

Fig. 1. SIM chromatograms and mass spectra of synthesized product and standard sample. (a) SIM chromatograms of the synthesized sample (top curve, for m/z 188) and the sample (m/z 136 and 188, lower curves) of the standard sample. The inset of the top curve shows a detailed view of the peak at $t_{\text{ret}} = 7.2$ min and the peak area (shaded) that was used for the quantification of adamantane. (b) Mass spectra acquired at $t_{\text{ret}} = 7.2$ min for the synthesized product (top) and a standard sample for the same retention time (bottom). The base peak at m/z 188 (labelled $M^{+\bullet}$) can be ascribed to the molecular ion of adamantane, whose molecular structure is displayed inside the mass spectrum of the standard sample. Synthesis conditions: $p = 5.84 \pm 0.02$ MPa; $T = 289.9 \pm 0.1$ K; $V_{\text{appl}} = 6.8$ kV_{p-p}; $f = 7$ kHz.

increase of the SIM peak areas increases following roughly a straight line, suggesting a linear relationship between the amount of dissolved precursor and the adamantane quantity. This also shows that larger amounts of precursors can help to increase the quantity of the synthesized product. However, it was observed that for much larger amounts of adamantane (on the order of $\sim 50 - 100$ mg), it became more difficult to ignite the plasma [21, 22], therefore the amount of precursor

Fig. 2. Evolution of the reaction yields of adamantane. (a) As a function of the amount of the precursor adamantane in the range of 1.0 to 13.4 mg (experimental conditions: $T = 290.0 \pm 0.1$ K; $p = 5.96 \pm 0.06$ MPa; $V_{\text{appl}} = 6.6 \pm 0.8$ kV_{p-p}). (b) For reaction times between 30 and 120 minutes and the following experimental conditions: $m(\text{Adamantane}) = 12.5 \pm 0.5$ mg; $T = 290.1 \pm 0.1$ K; $p = 5.93 \pm 0.03$ MPa; $V_{\text{appl}} = 6.4 \pm 0.4$ kV_{p-p}. For all data points, the integrated peak area corresponds to the peak acquired at a retention time of $t_{\text{ret}} = 7.2$ min.

cannot be increased to arbitrarily high values.

In Fig. 2(b), the variation of the SIM 188 peak area as a function of the plasma duration in the range of 30 to 120 min is shown. With increasing plasma duration, the intensity of the SIM peak area and hence the quantity of adamantane increases.

3.3 Sequential reaction model

In the following, we propose a simple model for the prediction of the reaction rates of diamondoids. We assume that diamondoids possessing a given cage number $n + 1$ (diamondoid D_{n+1}) form through the attachment of functional groups on the faces of a diamondoid with a lower given cage number, n (diamondoid D_n). For example, for the formation of adamantane ($n = 2$) from adamantane ($n = 1$), the reactions are expected to take place in a step-wise manner, that consist in the repeated removal of hydrogen terminations and attachment of alkyl radicals, which are formed by the dissociation of adamantane in the plasma.

Figure 3 shows a schematic of the suggested step-wise reaction mechanism to form adamantane ($n = 2$) from adamantane ($n = 1$). The reaction proceeds by re-

Fig. 3. Molecular structures of diamondoids considered for reaction model and possible stepwise reaction for the synthesis of diamondane. (a) Molecular structures of adamantane ($M_r = 136$, 4 faces), diamantane ($M_r = 188$, 6 faces) and triamantane ($M_r = 240$, 8 faces), and one of the three structural isomers of tetramantane, *iso*-tetramantane ($M_r = 292$, 10 faces). (b) Suggested reaction that consists in the subsequent repeated removal of hydrogen and the addition of methyl groups from adamantane (1), leading to the formation of 2-methyladamantane (3), 2,4-dimethyladamantane (5), 2,4,9-trimethyladamantane (7), and finally diamantane (8). The numbers 1 – 10 in structure (1) indicate the carbon sites for hydrogen removal and methyl attachment. The dots (•) in the intermediate structures (2), (4), and (6) and the hydrogen and methyl radicals symbolize unpaired electrons.

peated removal of hydrogen and attachment of methyl groups, which is similar to diamond film growth [27]. To be able to form diamantane from adamantane, the methyl groups have to attach to secondary carbons (positions 2, 4, 6, 8 and 9 in structure (1) of Fig. 3).

The change in the concentrations can be written as follows:

$$\frac{d[D_{n+1}]}{dt} = k_{n,n+1}[D_n] - k_{n+1,n+2}[D_{n+1}] \quad (1)$$

where $[D_n]$, $[D_{n+1}]$ are the concentrations and $k_{n,n+1}$, $k_{n+1,n+2}$ the reaction rate constants, with $n = 1, 2, 3, \dots$ the number of cages of a given diamondoid. The second part of equation (1) takes into account the loss of diamondoid D_{n+1} due to the formation of the next higher diamondoid, D_{n+2} . In the treatment that follows, because of the large amount, the concentration of the precursor adamantane, $[D_1]$, is assumed to remain constant, i.e. equal to its initial concentration at time $t = 0$, $[D_1]_0$:

$$[D_1] = [D_1]_0 = A_1 = \text{constant} \quad (2)$$

For the formation of diamantane from adamantane, equation (1) can be written as:

$$\frac{d[D_2]}{dt} = k_{1,2}[D_1] - k_{2,3}[D_2] \quad (3)$$

The differential equation (3) is solved using the following initial condition for diamantane: $[D_2]_0 = 0$. With this condition and using relation (2), the solution of (3)

can be written as:

$$[D_2] = \frac{k_{1,2}}{k_{2,3}} A_1 [1 - \exp(-k_{2,3}t)] \quad (4)$$

For diamondoids larger than diamantane ($n = 3, 4, \dots$), solving systems of differential equations analogous to equation (3) permits to calculate the corresponding variation in the concentrations. Since the diamondoid faces only allow specific sites for the attachment of new methyl groups, the reaction rates are assumed to be proportional to the number of possible attachment sites on the faces of the diamondoids. There are 4 equivalent faces for adamantane, 6 for diamantane, 8 for triamantane, and 10 for tetramantane. Consequently, the relationship between the reaction rate constants is assumed to be as follows:

$$k_{1,2} : k_{2,3} : k_{3,4} : k_{4,5} = 4 : 6 : 8 : 10 \quad (5)$$

where the reaction rate constants $k_{n,m}$, $n = 1, 2, \dots, n < m$ are the reaction rates corresponding to the formation of diamantane from adamantane ($k_{1,2}$), triamantane from diamantane ($k_{2,3}$) etc. In the present model, it is assumed that once diamondoids of a higher cage number $n + 1$ are formed, that the inverse reaction, i.e. the dissociation from a diamondoid with cage number $n + 1$ to a lower diamondoid, n , does not take place.

The evolution of the SIM peak areas corresponding to m/z 188 (diamantane), 240 (triamantane), and 292 (tetramantane), and which are proportional to the respective synthesized quantities, were fitted to the stepwise reaction model, under the constraints $k_{1,2} < k_{2,3} < k_{3,4} < k_{4,5}$. Figure 4 shows the experimental data points for the SIM peak intensity of diamantane, triamantane, and tetramantane as a function of the reaction time. As shown in the figure, the stepwise reaction model, displayed by the full curves in Fig. 4, is in agreement with the measured intensities. It also shows that the triamantane and tetramantane only appear once the diamantane concentration has started to increase. As can be seen in Fig. 4, the increase in the higher diamondoids is limited by the reaction rate of diamantane and therefore, the concentration of the next higher diamondoid $[D_n]$ is always lower than the next higher diamondoid, $[D_{n+1}]$.

The stepwise reaction model proposed here supports previous observations, e.g. in the stepwise elaboration of diamondane by conventional organic synthesis [28], and chemical-vapor deposition based synthesis processes of diamondoids [29], or the closed network growth of fullerenes [30], that also proceed in a stepwise manner. The current model still needs improvement, for example, for the moment, it does not take into account dissociation of a given diamondoids, D_n , to lower diamondoids, D_{n-1} , $D_{n-2} \dots$, that might occur if the formed diamondoids are exposed to the plasma too long. However, the proposed model permits to reproduce the experimental observation, i.e. that diamondoids starting from triamantane, tetramantane etc.

Fig. 4. Evolution of the diamondoid formation. The symbols are the peak intensities corresponding to diamantane (SIM 188, circles), triamantane (SIM 240, squares) and tetramantane (SIM 292, lozenges) as a function of time. The curves through the experimental data points are the fits of the reaction rate model.

can only form once the formation of diamantane has initiated and that the concentrations of diamondoids with a higher cage number will be smaller than those of the next lower diamondoid.

4. CONCLUSIONS

We have investigated the synthesis of diamondoids by dielectric barrier discharges generated in supercritical xenon. The synthesized products were analyzed qualitatively and quantitatively using gas chromatography - mass spectrometry. The mass spectra indicate the synthesis of diamantane, triamantane, and tetramantane. The reaction yield of diamantane increases with increasing precursor concentration and plasma generation time. A simple reaction model that assumes that larger diamondoids grow in a stepwise manner shows that diamondoids with a given cage number $n + 1$ only grow once diamondoids with $n - 1$ have been formed. Consequently, to be able to grow higher diamondoids, it is necessary to provide alkyl radicals that allow stepwise growth and establish conditions where diamondoids do not break apart again once they are formed.

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