Buckybomb: Reactive Molecular Dynamics Simulation

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ABSTRACT: Energetic materials, such as explosives, propellants, and pyrotechnics, are widely used in civilian and military applications. Nanoscale explosives represent a special group because of the high density of energetic covalent bonds. The reactive molecular dynamics (ReaxFF) study of nitrofullerene decomposition reported here provides a detailed chemical mechanism of explosion of a nanoscale carbon material. Upon initial heating, C60(NO2)12 disintegrates, increasing temperature and pressure by thousands of Kelvins and bars within tens of picoseconds. The explosion starts with NO2 group isomerization into C=O=N=O, followed by emission of NO molecules and formation of CO groups on the buckyball surface. NO oxidizes into NO2 and C60 falls apart, liberating CO2. At the highest temperatures, CO2 gives rise to diatomic carbon. The study shows that the initiation temperature and released energy depend strongly on the chemical composition and density of the material.

Development of novel nanoscale materials has boosted a number of innovative research areas, including electronics, engineering, and biotechnology.1–3 Carbon structures and high-energy systems constitute two particularly interesting classes of nanomaterials. The first class, which includes graphene, nanotubes, and fullerenes, has been extensively studied during the last 2 decades. Applications of nanoscale carbon range from solar cells to anticancer therapy.4–14 In turn, high-energy nanomaterials constitute a new promising field. Several important developments, such as nanoscale explosives, have been recently reported. The potential applications of nanoscale explosives extend beyond military purposes and industrial processes.15–18

Interplay of the unique properties of both classes—carbon structures and energetic nanomaterials—can lead to development of revolutionary and highly energetic carbon compounds. The field on nanoexplosives is fresh, requiring breakthrough developments of robust and less toxic materials. In this sense, carbonaceous materials exhibiting structural diversity provide an exceptional platform for the development and research of reactive energetic systems.2 Chemical methods have proven to be extremely efficient in changing the properties of fullerenes and nanotubes via covalent or noncovalent functionalization.19,20 In particular, the horizon of the C60 fullerene applications has been significantly extended by chemical modifications of its structure.21

Polynitrofullerenes are stable molecules with a high energy of formation. Their synthesis has been recently reported22,23 while prospective applications have been barely researched yet. The NO2 group is well-known as a major source of oxygen, which contributes strongly to detonation and combustion processes via partial or full oxidation of intermediate products.24 One would expect that nitrated fullerenes could emerge as promising nanoexplosives, whose power and sensitivity can be tuned.

The present work simulates a real-time explosion of dodecanitrofullerene, C60(NO2)12, which we nickname a buckybomb. Reactive molecular dynamics (ReaxFF) is used to establish, for the first time, a detailed mechanism of explosion of a nanoscale carbon material. The study shows that upon initial heating to 1000 K, the NO2 groups isomerize into C=O=N=O groups within 1 ps. Rapidly after that, NO molecules are emitted, and CO groups are formed on the buckyball surface. Finally, both NO and C60 are oxidized. NO gas becomes NO2 gas on a sub-10 ps time, and C60 disintegrates, producing CO2. The C60 disintegration continues for tens of picoseconds. The temperature and pressure grow by thousands of Kelvins and bars. At the highest temperatures, 100 ps after the start of the explosion, CO2 gives rise to diatomic carbon. The established time-resolved chemical transformations provide a unique perspective on the nanoscale explosion process, generating insights that can be used to design novel energetic materials.

The first nine NO2 groups were attached to C60 in such a way that every hexagon and pentagon contained a single NO2 group. The additional three NO2 groups were attached to random carbon atoms. The total number of NO2 groups was selected to attain a balance between stability at room conditions and vigorous explosion upon initiation. Smaller numbers of NO2 groups, in particular, six and nine, were preliminarily tested. According to Cataldo and co-workers,22 C60(NO2)14 can be experimentally obtained. This compound is unstable.

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however. To increase stability, we decreased the number of nitro groups.

The nonequilibrium explosion dynamics were simulated in the following way. The potential energy of each system was minimized using the conjugate gradient algorithm for geometry optimization. The resulting configurations correspond to local energy minima in the absence of thermal motion. Afterward, the systems were heated to 1000 K. The classical equations of motion were propagated conserving the total energy. Figure 1 depicts the evolution of temperature and pressure during the simulated explosions. The reported pressure is closely related to the detonation pressure. The nearly linear dependence of pressure on density indicates that the explosion is largely an intramolecular reaction. Temperature evolution is shown up to 4000 K because energy conservation at higher temperatures is unstable even with a 0.1 fs time step. In turn, higher temperatures cannot be easily achieved upon real conditions because of inevitable energy dissipation. For instance, a polynitrofullerene is exploded under either N2 or air in the recent experiments,22 and excessively high temperatures are not observed. The surrounding gas provides a heat bath that accommodates the excess energy released during the explosion.

For explosion to happen, an initiation event must take place. This event can include an exothermic reaction with a low-energy barrier or mechanical impact. In case of a buckybomb, such a reaction is isomerization of C−NO2 groups into C−O−N−O groups (Figure 2). The homolysis reaction is the primary fission process of nitroaromatic compounds under thermal, impact, shock, and electric spark initiation stimuli.25 This is consistent with the recent experiments on polynitrofullerene explosion.22 The unimolecular nitro to nitrito isomerization has a relatively low barrier; however, it is entropically unfavorable and occurs at high temperatures. The reaction takes place within 1 ps and results in a temperature increase from 1000 to 2500 K (Figure 2). This stage does not depend on the explosive density because it is an intramolecular chemical reaction. The energy released during the explosion can be increased by adding more NO2 groups, for instance, as in C60(NO2)14.22 Octanitrocubane, containing one nitro group per carbon atom, is extremely energetic.26

The temperature of 2500 K is sufficient to initiate partial decomposition of C60(NO2)12. A certain fraction of NO and NO2 molecules (Figure 3) leaves the major particle, fostering formation of carbonyl groups, C=O. Additional C=O groups are formed at the buckyball surface due to interaction with molecular oxygen. The NO gas is unstable at 2500 K. It reacts with oxygen within a very few time steps to form NO2, in agreement with experimental knowledge. Formation of carbonyl groups is the first step toward oxidation. This stage is fast.
The carbonyl groups make the buckyball highly unstable at ~3000 K. A significant fraction of carbon atoms break carbon–carbon bonds and join CO₂ molecules (Figure 3). A higher content of oxygen-containing reactants in the system would increase the reaction rate even further.

Starting from ~4000 K, carbon–carbon bonds are broken quickly. This process releases the main portion of energy, which is responsible for a huge pressure elevation (Figure 1). The simulations were stopped at this stage because drastic kinetic energy increase during the reaction makes the integration time step of 0.1 fs insufficiently small to conserve the total energy. Therefore, temperature and pressure computed above the carbon–carbon bond decomposition temperature are insufficiently reliable. The system state at these very high temperatures is not reported.

The final mixture (Figure 4) is composed primarily of CO₂, NO₂, N₂ gases, and linear carbon chains. NO and O₂ gases are absent because NO was oxidized to NO₂ and O₂ formed carbon dioxide molecules with carbon atoms. The molecular nitrogen is at a lower state of internal energy than the oxides of nitrogen. This is why a significant number of nitrogen atoms exist as N₂ at the end of reaction. The presence of significant amounts of NO₂ gas is expected because homolytic dissociation of C–NO₂ bonds is the primary fission process of nitroaromatic compounds under thermal, impact, shock, and electric spark initiation stimuli. Interestingly, despite an excess of carbon atoms, CO₂ dominates over CO. Note that the composition of the final mixture depends on available atoms, determined by the initial composition of each simulated system. For instance, the presence of hydrogen, whether in the form of molecular hydrogen or water vapor in the initial mixture of reactants, would result in formation of hydrocarbon chains. A larger fraction of oxygen molecules would promote carbon chain oxidation into carbon dioxide. This combustion reaction is known to be exothermic.

The time step used for integration of equations of motion is a central parameter in constant-energy MD simulations. It influences the validity of all results, being responsible for total energy conservation. The reactive MD method, in the form applied in this work, does not employ schemes for interaction energy cutoff, as is done customarily in conventional MD simulations. Therefore, energy conservation depends on the integration of Newton equations and accuracy of numerical procedures for energy calculation. Figure 5 provides a comparison for different time steps. Simulation of reactions at the elevated temperatures requires significantly smaller time steps than those usually applied in the nonreactive simulations (1–5 fs). On the basis of the performed analysis, we selected a 0.1 fs time step, which achieves reasonable balance between accuracy and computational costs.

To recapitulate, we have reported nonequilibrium reactive MD simulations of a C₆₀(NO₂)₁₂ buckybomb explosion. We have shown that this compound exhibits properties of a highly energetic material. Heated to 1000 K, C₆₀(NO₂)₁₂ decomposes spontaneously, providing a significant amount of heat. The heat is released due to a high density of covalent energy stored by carbon–carbon bonds. NO₂ groups act as explosion initiators, providing an initiating portion of kinetic energy (temperature increase) to the system. Because surroundings are not required to initiate the explosion, the buckybomb explosive can be used in any media. Atmospheric oxygen actively participates in this reaction after the initial stage. The decomposition mechanism has been elucidated in detail. The rates of all elementary steps and the nature of the transient species have been established, and the reaction products have been discussed. Because the NO₂ groups attached to the fullerene initiate the reaction, the number of such groups can be used to control the explosion. The linear dependence of the explosion pressure on the polynitrofullerene density indicates that explosion strength can be modified by changing the compound concentration. Fast liberation of chemical energy, resulting in a 3000 K temperature increase within 50–200 ps, provides exciting opportunities for chemistry and engineering.

**METHODOLOGY**

The molecular dynamics (MD) simulations were performed using a quantum chemistry (QC)-based reactive force field (ReaxFF). The parameters were thoroughly trained using a variety of carbon-, nitrogen-, and hydrogen-containing compounds. This methodology was applied previously with success to address a number of complicated problems including the explosive behavior of TNT and the initial reaction of coal pyrolysis. ReaxFF provides a reliable
description of reactive potential surfaces for many-particle systems. The method treats all atoms in the system as separate interaction centers. The instantaneous point charge on each atom is determined by the electrostatic field due to all surrounding charges, supplemented by the second-order description of dE/dq, where E is the internal energy and q is the electrostatic charge on a given atom.27,28 The interaction between two charges is written as a shielded Coulomb potential to guarantee correct behavior of covalently bonded atoms. The instantaneous valence force and interaction energy between two atoms are determined by the instantaneous bond order. The latter is determined by the instantaneous bond distance. These interaction energy functions are parametrized versus QC energy scans involving all applicable types of bond-breaking processes. The bond order concept is used to define other valence interactions, such as bond, lone electron pair, valence angle, conjugation, and torsion angle energies. It is important for energy conservation and stability that all interaction terms smoothly decay to zero during bond dissociation. The conventional pairwise van der Waals energy term describes short-range electron–electron repulsion, preserving atom size, and longer-range London attractive dispersion. Unlike non-reactive MD simulations, ReaxFF uses the van der Waals term for covalently bonded atoms, where it competes with a monotonically attractive bond term. Such an approach to chemical bonding requires a significant number of independent parameters, which can be obtained from QC energies. Bond dissociation, geometry distortion, electrostatic charges, infrared spectra, equations of state, and condensed-phase structures are typically derived using an electronic structure method, such as density functional theory, to be subsequently used in the ReaxFF parametrization. The works by van Duin, Goddard, and co-workers27,28 provide a more comprehensive description of the methodology used here. The simulations were performed using the ADF2012.01 code, available through scm.com.

The list of the simulated systems is given in Table 1. Each system was simulated during 500 ps with an integration time step of 0.1 fs. The explosion simulations were carried out in the constant energy ensemble (NVE), while the induced pressure was determined in the constant volume–constant temperature (NVT) ensemble. Initial molecular configurations were generated using the PackMol26 procedures to obtain system energies close to local minimum (see Figure 6). The system geometry was optimized. Subsequently, the system was rapidly heated in the NVT ensemble to 1000 K at the rate of 10 K per ps, without reactive terms in the potential. NVE simulations were started at 1000 K, and the system temperature was monitored until the explosive decomposed into individual atoms (∼5000 K). Fifteen oxygen molecules were added to each system (Figure 1) to represent oxidants in the atmosphere generally because they are anticipated to play an important role in the explosion kinetics.

![Figure 6. Starting configurations of the simulated systems. The unit box for the higher-density systems is depicted in gray. Carbon, nitrogen, and oxygen atoms are gray, blue, and red, respectively. Each system contains 15 O2 molecules to represent an atmosphere. The O2 molecules are made invisible in the isolated C60(NO2)12 system for clearer representation of the explosive structure.](image)

The algorithm of fragment recognition uses connection table and bond orders calculated at every time step. The bond order cutoff used to identify molecular species is set to 0.3 for all bond types. Two fragments are considered separate molecules if all bond components, defined between them, exhibit orders smaller than 0.3. Note that the definition of a chemical bond is not unique, in principle. The selected value of the bond order cutoff influences the composition and concentration of intermediate products, but it does not influence the final (stable) products. Consequently, ReaxFF sporadically suggests existence of certain exotic molecules and fragments, which are not detected by any experimental technique because of their transient nature and low stability. It is important to distinguish between bonded and nonbonded atom pairs in order to obtain translational kinetic energy, which is converted into temperature. The selected value (0.3) was tested in previous works, showing reliable and chemically sound results.

High-temperature chemistry involves excited electronic states. Empirical force fields, however, do not include excited states in the parametrization procedures for technical reasons. Therefore, the simulated dynamics and chemical reactions correspond to the ground state of the polynitrofullerene. Even though excited states are not considered explicitly, all major reported results are in line with the chemical expectations. The decomposition of the buckybomb agrees with the results of the Born–Oppenheimer MD simulations on nitromethane distributed between graphene sheets.

### Table 1. Simulated Systems and Representative Results

<table>
<thead>
<tr>
<th>C60(NO2)12</th>
<th>Number of bonding interactions</th>
<th>Density, kg m⁻³</th>
<th>Time before decomposition, ps</th>
<th>Number of independent simulations</th>
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<td>1</td>
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The authors declare no competing financial interest.

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