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First-Principles Simulation of Highly Reactive Systems: Immediacy on a Femtosecond Time Scale

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Using Car-Parrinello molecular dynamics we study the first reaction steps of the decomposition of a nitrogen-rich molecule and of a mixture of molecular oxygen and molecular hydrogen. Using the simulated-annealing approach we increase the temperature of the systems till they start to react. Both systems have in common that they react violently and that the precise reaction pathways, respectively the single reaction steps under the chosen conditions are largely unknown. While the first system decomposes completely within some hundred

femtoseconds, the latter mixture reacts only partially on this timescale due to entropy. Complex reaction chains involving up to ten hydrogen and oxygen molecules allow for a fast reaction, but require a very specific arrangement. To our knowledge such reaction chains of neutral, stable, ground state molecules were not described before. The hope for a decomposition to nitrogen respectively to water is essentially fulfilled, but side products are observed.

Motivation

High energy materials are interesting for energy storage, transport and controlled decomposition. Two aspects have been discussed as being important in recent years, namely a high kinetic barrier to decomposition and environment-friendliness of the products. The kinetic hinderance is important for a safe handling. Recently, a C_2N_{14} compound was synthesized and characterized by the group of Klapötke.^[1] Not many of such binary compounds consisting of carbon and nitrogen only, have been synthesized so far. Most recently a fascinating C_8N_{26} compound was synthesized.^[2]

For the C_2N_{14} system under consideration in this study it was possible to prepare crystals and to analyze the structure. In the present paper we study the decomposition of the crystal and compare it to the decomposition of a mixture of molecular oxygen and molecular hydrogen at hypercritical conditions. We ask the question what are the reaction pathways and intermediates. Comparing the single reaction steps for both systems, we ask how well chemical intuition works on the picosecond timescale. We will find that the two highly reactive systems follow different reaction schemes. Particularly for the $H_2 + O_2$ system, reaction mechanisms are observed which were not discussed before.

The quantum mechanical investigation of the reaction mechanism of H_2 and O_2 has a long history, probably starting

with the study of Bear and Eyring.^[3] Many kinetic studies have been published since then, see for example Refs.^[4] and^[5] and papers cited therein. Way less is known about the dynamics of the reaction. Using Car-Parrinello molecular dynamics (CPMD)^[6,7, 8] it is possible to simulate arbitrary chemical reactions 'on-the-fly'. This means that the Kohn-Sham equations are only solved for the points which are reached during the simulation instead of computing complete potential energy surfaces in advance of doing dynamics. The on-the-fly approach is superior to traditional quantum chemical PES (potential energy surface) calculations if the reaction pathways are complex and/or completely unknown. The background for reliable simulations is the use of density functional theory^[9] in the Kohn-Sham formalism^[10] in combination with gradient corrections^[11,12] and dispersion corrections.^[13] The CPMD approach is similar to Born-Oppenheimer molecular dynamics (BOMD), except that in the latter the electron cloud is fully optimized to the Born-Oppenheimer surface in every time step using the Kohn-Sham equations. In the CPMD approach a force is obtained from the deviation of the Kohn-Sham solution from the Born-Oppenheimer surface. This force moves the wavefunction in every time step according to the Car-Parrinello equations. For this motion, the electronic system is given a fictitious mass.^[7] In both CPMD and BOMD the nuclei are moved classically in every time step. The disadvantage of both approaches is the short simulation times and the limited system sizes. To bridge this gap we use the simulated annealing technique which means that we multiply the temperature with a factor slightly larger than one in every time step till we observe a reaction. There are many alternative ways to investigating chemical reactions using molecular dynamics or related techniques: Among the oldest are umbrella sampling^[14] and the nudged elastic band method.^[15] Both afford the knowledge of the intermediate or product, hence they are hardly applicable to the systems investigated in this study. The same is true for chemical flooding^[16] and

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metadynamics^[17] where the reactivity is changed in the direction of selected variables. We also make no use of a nano reactor as developed by Martinez et al.^[18] Since we have periodic boundary conditions we do not have the problem that the reactants may fly away from each other instead of reacting. In a sense, our simulation cell serves as a nano reactor but with periodic boundary conditions. An approach similar to ours was chosen by Martinez-Nunez in Ref.,^[19] except that way higher kinetic energies were used in that study. Our aim is not to find all possible isomers, but the most likely reaction pathways. The increase of the temperature is a relatively unbiased way of making a system react. Any combination of internal coordinates can make up a reaction coordinate. What is problematic in simulated annealing simulations is that the entropy is only partially taken into account as our simulation times are too short. Reactions that afford a very special arrangement of the molecules occur less likely in our simulations.

However, we will show in the present study that it is not excluded to observe such situations.

We find an immediate decomposition for the C_2N_{14} crystal at high temperatures and an entropically more strongly

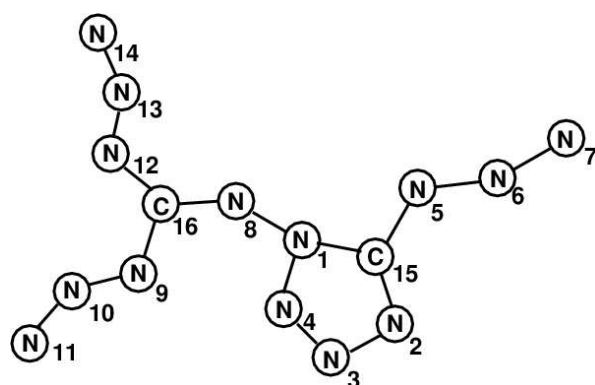


Figure 1. The numbering of the isolated C_2N_{14} compound.

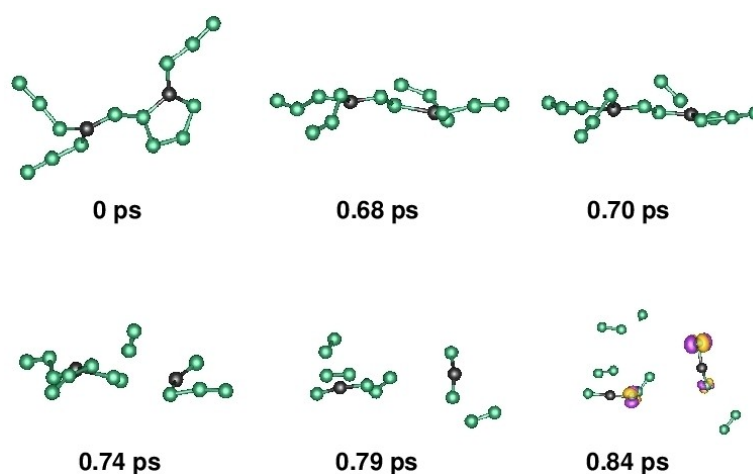


Figure 2. Snapshots of the decomposition of a single C_2N_{14} molecule. In the first reaction step the ring is broken. The consecutive reaction steps produce molecular nitrogen and NCN biradicals. The radical character is shown by plotting the spin densities.

hindered reaction for $H_2 + O_2$. Our results enrich the number of possible reaction pathways for the reaction of H_2 and O_2 .^[20–24]

Results and Discussion

C_2N_{14}

Initially we investigated isolated C_2N_{14} molecules (Figure 1).

Upon heating they decompose at a temperature of about 2000 K. This high temperature is caused by our high heating rate. Experimentally the substance decomposes at about 380 K. In the simulations the reaction always starts in the same way (see the movie *c2n14.1.mpg* and the trajectory file *c2n14.1.xyz* in the Supplementary Material): First the N_1-N_4 bond is broken, that is, the five membered ring is broken resulting in a symmetric structure. Both carbon atoms have now the same substituents namely two azide moieties each and they are connected via two nitrogen atoms. This structure does not yet have radical character (Figure \ref{1e}). Also the next step does not yet generate radicals: One of the four azide rests dissociates in order to yield molecular nitrogen. Then one of the bonds of the nitrogen bridge in the middle of the molecules is broken. This continues till only molecular nitrogen and mainly NCN biradicals are left. These biradicals are certainly highly reactive, but on a longer timescale than that of our simulations. Figure 3 shows the development of energies, temperature and bond lengths with time. The first bond breaking is observed for the N_1-N_4 bond plotted in black. This is immediately followed by the dissociation of the N_2-N_3 bond plotted in red. All further decomposition steps occur within about 0.2 ps. The reaction is connected with a relatively sudden jump in energy and temperature (Figure 3). The energy and temperature continue to raise after the reaction. Also the fictitious kinetic energy of the electrons raises to some degree, which is unavoidable during a rapid reaction in which the electrons must move quickly.

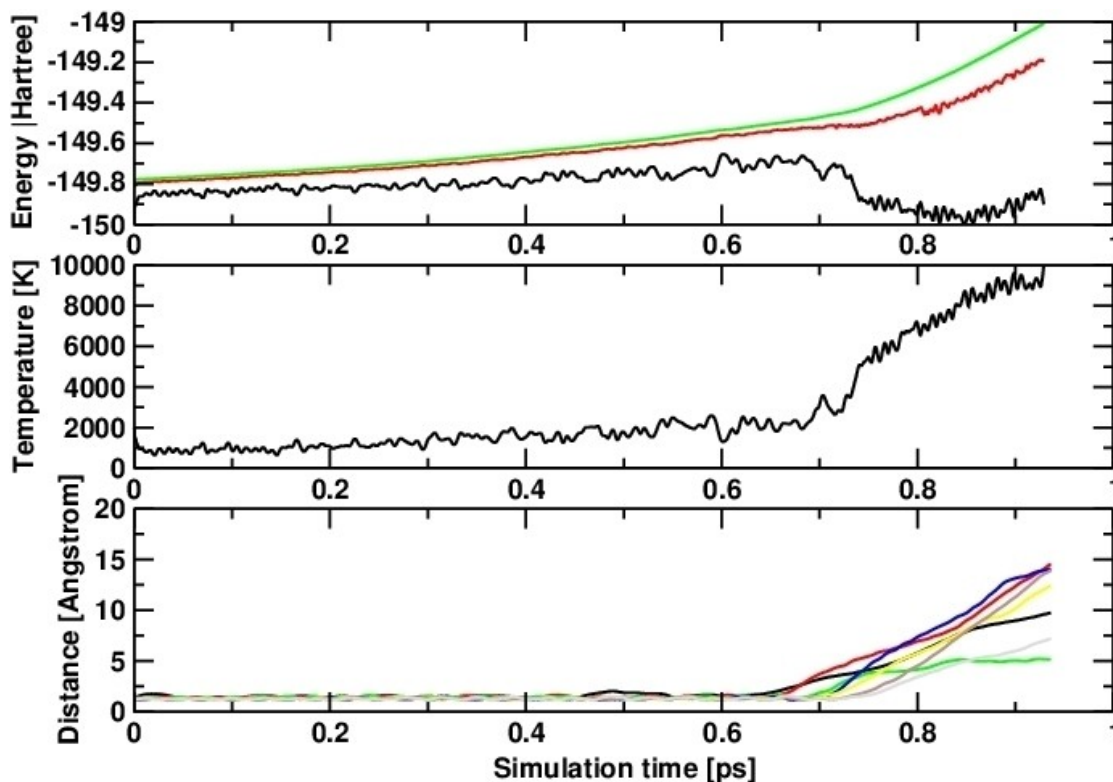


Figure 3. Energetics and change of distances during the decomposition of a single C_2N_{14} molecule. (Upper plot: black: Kohn-Sham energy, red: classical energy including kinetic energy of the ions, green: conserved total energy including the fictitious kinetic energy of the electrons; lower plot: black: N_1-N_4 , red: N_2-N_3 , green: N_1-C_{15} , blue: N_5-N_{10} , yellow: N_6-C_{16} , brown: N_5-N_6 , grey: $N_{12}-N_{13}$.) In the first reaction step the five-membered ring is opened (N_1-N_4 bond, black line). This is immediately followed by the dissociation of the N_2-N_3 bond leading to a dissociating nitrogen molecule (red line). The next steps occur essentially at the same point in time, that is, within one vibrational period.

In addition we performed calculations for the crystalline form with eight molecules in the simulation cell (Figure 4).

The result does not add much to the simulation of a single molecule, except that the outcome is more chaotic (see the movie *c2n14.8.mpg* and the trajectory file *c2n14.8.xyz* in the Supplementary Material; the trajectory file *c2n14.8molecules.-xyz* shows the same trajectory, but with a different application of the periodic boundary conditions). Again the first reaction step is the breaking of one of the N_1-N_4 bonds, and again the complete decomposition is almost immediate. The energy raises continuously which is explained by the breaking of many bonds on the picosecond time scale. Again NCN biradicals are formed. Besides that bigger fragments remain. Also the formation of carbon-carbon bonds from highly reactive fragments is observed. In the simulation run shown in Figures 5 and 6 mainly molecular nitrogen is left after 1.35 ps. Our simulations are constant volume simulations. The formation of gaseous nitrogen molecules leads to a quick expansion in experiment, which should prevent the condensation to bigger structures.

The radical character is shown by plotting the spin densities. It is strongest in the middle of the reaction.

$H_2 + O_2$

We performed simulations for 20 oxygen and 40 hydrogen molecules as well as for 32 oxygen and 64 hydrogen molecules, for the simulation protocols see the Supplementary Material. As oxygen and hydrogen are gaseous under the chosen conditions, this corresponds to a situation under very high pressure. Several reaction conditions have been tested. Some of the successful, i.e., reactive simulations were analyzed in full detail. Generally we observe a strong decrease of reactivity if Nose thermostats are applied to the electrons. To check if the reactivity depends on the deviation of the system from the Born-Oppenheimer surface, we did additional calculations using the more expensive Born-Oppenheimer molecular dynamics. These simulations confirm that the reaction would also occur if the wavefunction is optimized to the potential energy surface in every step.

In a simulation with 20 oxygen and 40 hydrogen molecules two different reaction chains are observed, one leading to OOH radicals only (Figure 7), the other leading to water amongst other products (Figs. 8 and 9). A movie is provided in the Supplementary Material (*h2+o2.40.mpg* and *h2+o2.40.xyz*). What is striking in the movie is the fact that the light hydrogen molecules rotate very fast and almost freely while the oxygen molecules hardly move. In spite of this fast motion of

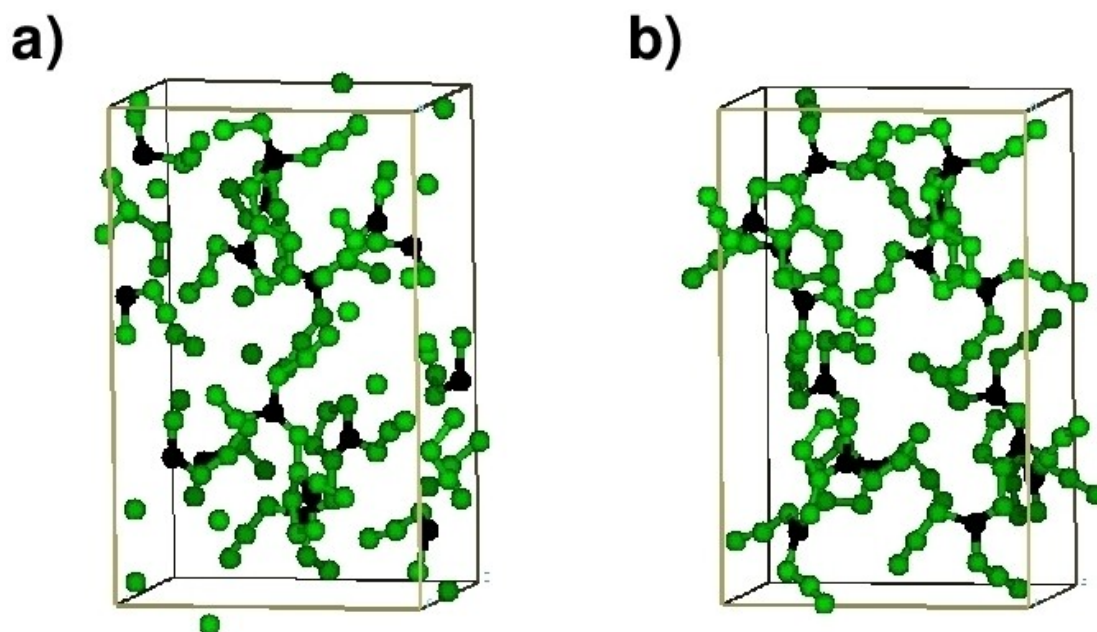


Figure 4. Crystal structure of C_2N_{14} . The orthorhombic cell contains eight molecules. a) Experimental structure.^[1] b) Same structure but using periodic boundary conditions to generate integral molecules.

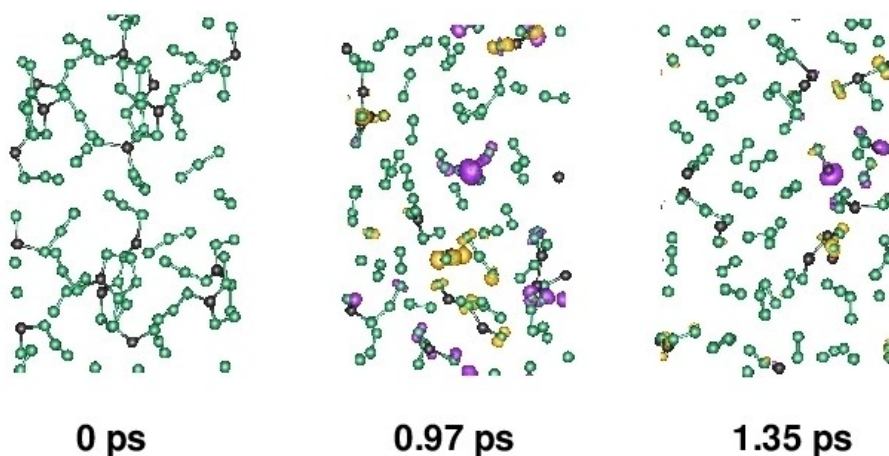


Figure 5. Snapshots of the decomposition of a C_2N_{14} crystal. In the first reaction step a ring is broken. The consecutive reaction steps produce molecular nitrogen and several radicals containing carbon atoms.

the hydrogen molecules it is possible that they suddenly arrange in reaction chains, which causes a freezing of this fast nuclear motion during the reaction.

In one of the simulation runs with 32 oxygen and 64 hydrogen molecules we observed a remarkable mechanism. Water was formed when all four lone pairs of a hydrogen molecule were coordinated by hydrogen molecules. For such a configuration, water formation can be immediate. In a quick row of reaction steps four water molecules and two OOH-radicals are formed. For the first pair of water molecules all four O–H bonds are formed simultaneously (red bonds in Figure 10). Three hydrogen molecules are involved in this reaction step: One hydrogen molecule coordinates with both atoms to the

oxygen molecule. The other two hydrogen atoms stem from different hydrogen molecules. At the same time the O–O bond is broken (Figs. 10 and 11).

The second pair of water molecules is formed in a somewhat different fashion: One of the four hydrogen atoms which are now bound to the first pair of water molecules breaks its bond to the other hydrogen atom. Less than 0.1 ps after the reaction of the first pair of water molecules, it forms a bond to the next oxygen molecule close by. This leads to the elongation of the O–O bond, but this bond is not yet breaking. Soon later, however, the other side of this oxygen molecule is attacked at both lone pairs by yet another hydrogen molecule and two O–H bonds are formed. This leads to oxygen dissociation. The

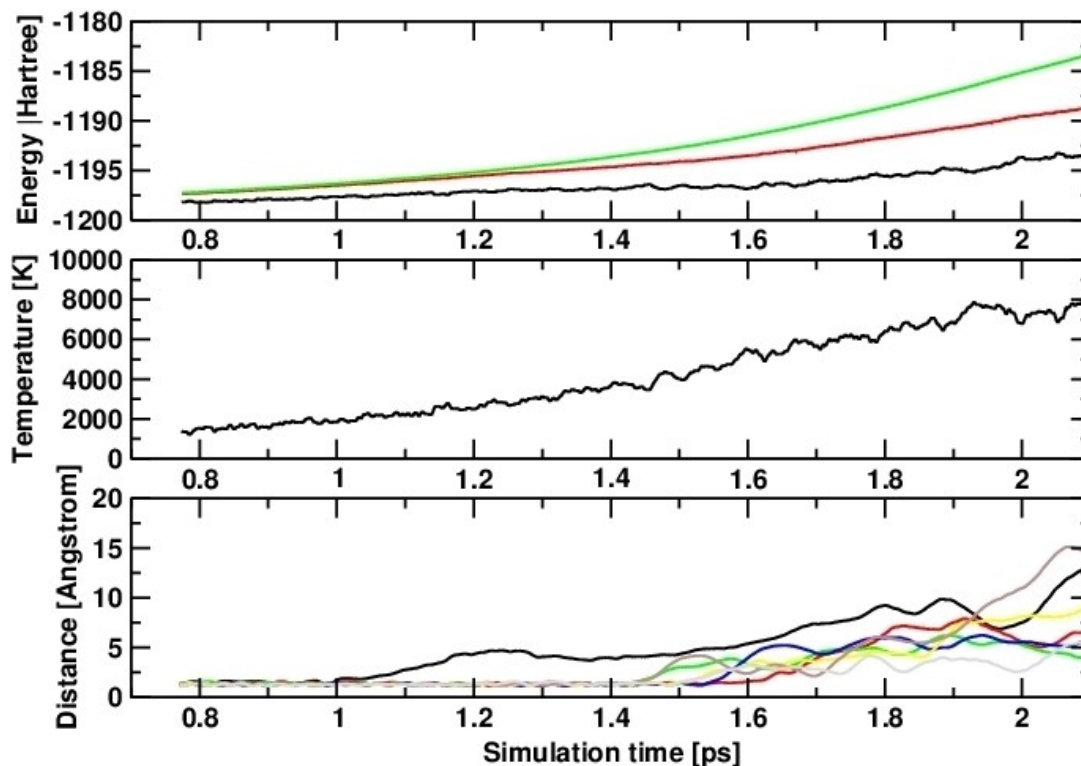


Figure 6. Energetics and change of distances during the decomposition of a C_2N_{14} crystal. (Upper plot: black: Kohn-Sham energy, red: classical energy including kinetic energy of the ions, green: conserved total energy including the fictitious kinetic energy of the electrons; lower plot: black: N_1-N_4 , red: N_2-N_3 , green: N_1-C_{15} , blue: N_5-N_{10} , yellow: N_8-C_{16} , brown: N_5-N_6 , grey: $N_{12}-N_{13}$.) In the first reaction step the five-membered ring of one of the eight molecules in the unit cells is opened (N_1-N_4 bond, black line). After 0.4 ps this is followed by the dissociation of the N_1-C_{15} and the N_5-N_6 bonds (green and brown curves). The next steps occur almost simultaneously.

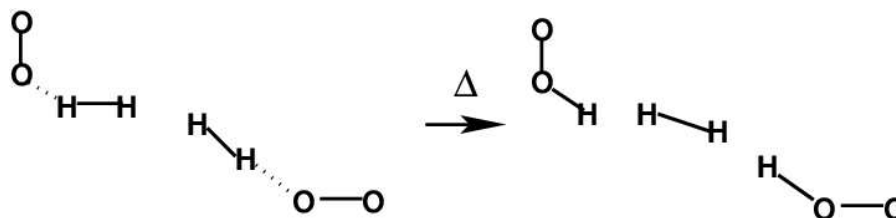


Figure 7. Sketch of one of the reaction chains in the simulation of 20 oxygen and 40 hydrogen molecules in one simulation cell at high temperatures. In the first series of nearly simultaneous bond breaking events, OOH radicals and one hydrogen molecule are formed.

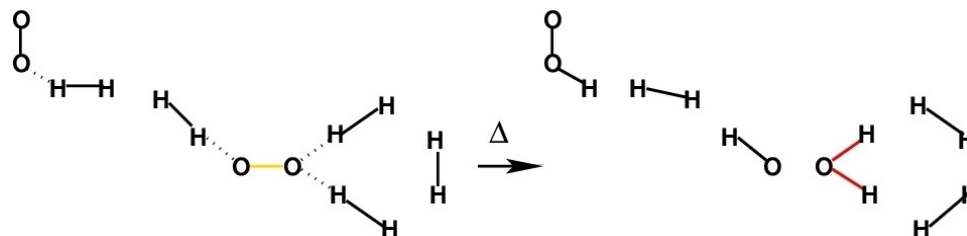


Figure 8. Sketch of another reaction chain in the simulation of 20 oxygen and 40 hydrogen molecules in one simulation cell at high temperatures. In this second series of reaction steps, two oxygen molecules and five hydrogen molecules react to one water molecule, one OH radical, one OOH radical, and three hydrogen molecules.

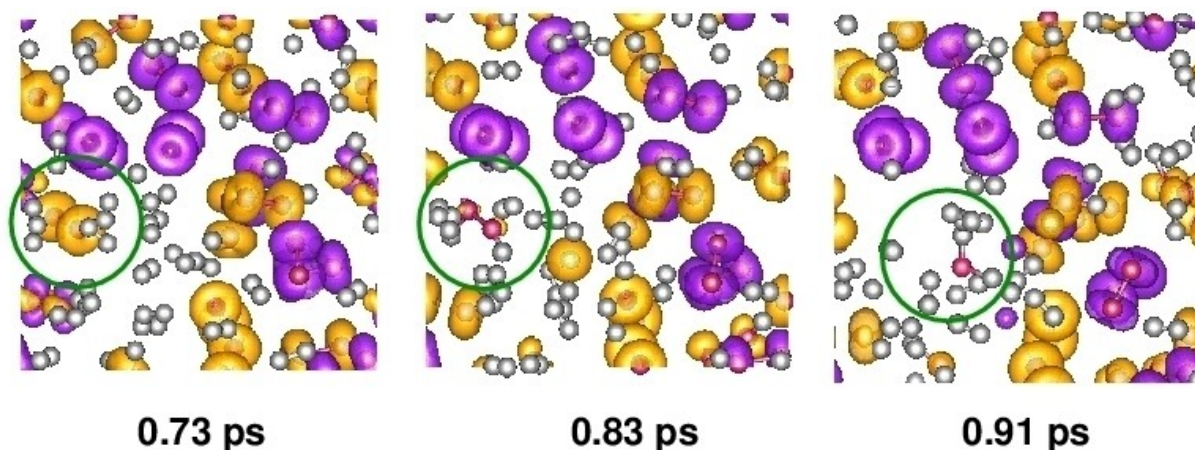


Figure 9. Snapshots of the reaction in the simulation of 20 oxygen and 40 hydrogen molecules in one simulation cell at high temperatures. Where water is formed, the spin density disappears.

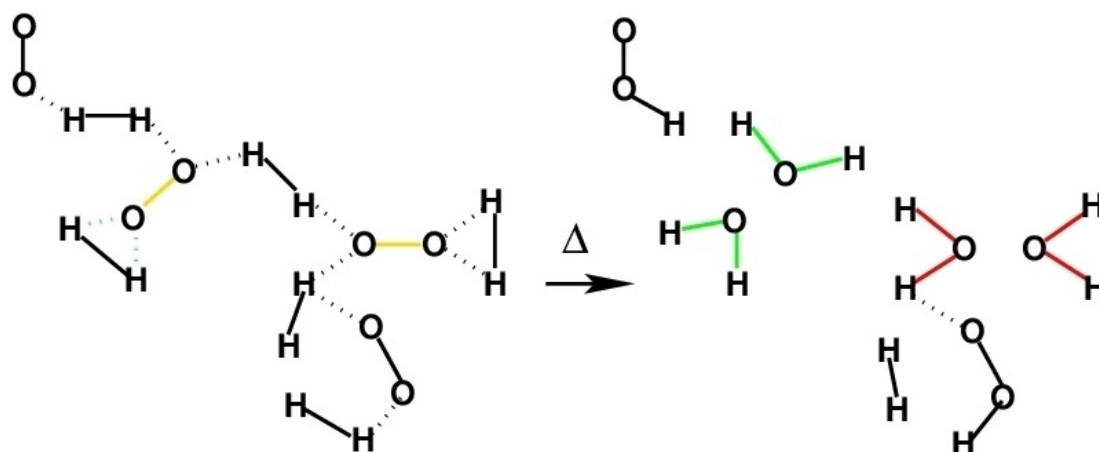


Figure 10. Mechanism of the start of the water formation from 32 oxygen and 64 hydrogen molecules at high temperatures. In total five hydrogen molecules attack two oxygen molecules and break the two O–O bonds (orange). Two more oxygen molecules and one more hydrogen molecule are involved in the total reaction. The reaction starts with the formation of the red bonds. This reaction step is analysed in Figure 11. The second pair of water molecules (green bonds) is formed a little later (Figure 12).

last reaction step leads to the formation of the fourth water molecule 0.6 ps later (Figure 12).

In contrast to the decomposition of the C_2N_{14} crystal, the reaction of H_2 and O_2 does not lead to an immediate reaction of all components at the picosecond timescale, as it is entropically strongly hindered. In any case, the number of molecules in a reaction chain is reduced by the reaction. Hence, the reaction becomes more favourable at higher pressure. Under constant volume conditions, also an endothermic reaction can occur. (For the energetics see the Supplementary Material).

Conclusions

We have found two different behaviours for the decomposition of the C_2N_{14} crystal and for the water formation. The C_2N_{14} crystal shows hardly any motion till a temperature of 2000 K is

reached. Above that point the decomposition becomes violent and all of a sudden nitrogen molecules are formed. The highly exothermic reaction leads to extreme temperatures of 10000 K and above. Besides nitrogen mainly NCN biradicals remain which are metastable on the timescale of the simulation. In contrast every step of the water formation is kinetically hindered. Only for a very particular arrangement of the H_2 molecules around an O_2 molecule, a reaction is observed. This leads to reaction chains which resemble proton wires in the case of a Grotthuss mechanism, except that our reaction chains are not charged, but start from neutral, stable molecules. Typically three hydrogen molecules arrange in a way that every lone pair of oxygen is attacked simultaneously. The reaction involving the breaking of the O–O double bond is then immediate. Hence we observe a large entropic barrier. Amongst other side products the highly reactive OOH radical is predominant on the timescale of our simulations. Its formation

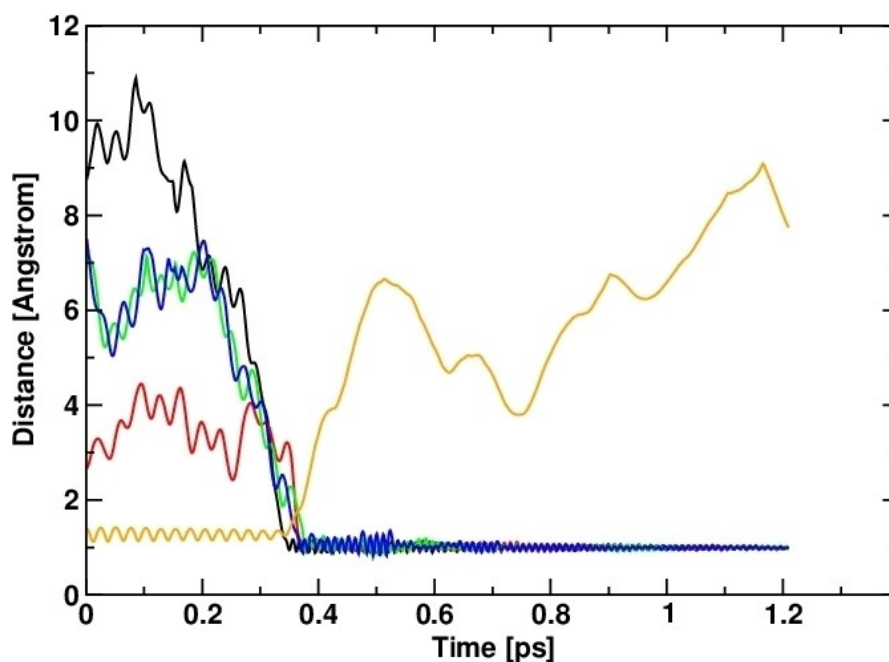


Figure 11. Change of distances during the reaction of O_2 and H_2 (32 oxygen and 64 hydrogen molecules), first series of reaction steps. Four O–H bonds (red in Figure 10) are formed simultaneously and at the same time the O–O bond (orange, also orange in Figure 10) is broken.

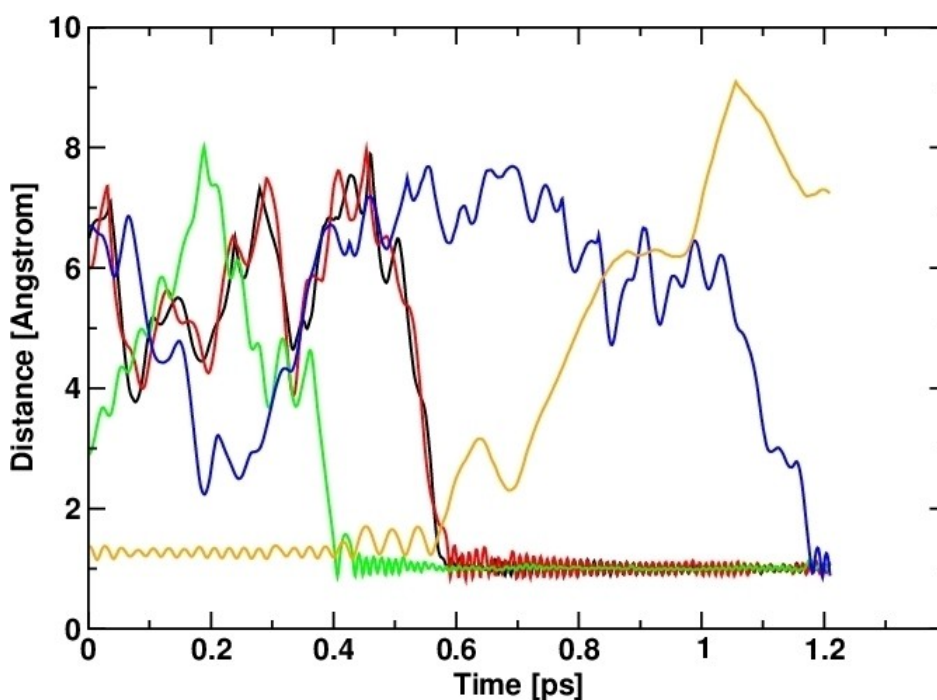


Figure 12. Change of distances during the reaction of O_2 and H_2 (32 oxygen and 64 hydrogen molecules), second series of reaction steps. Four O–H bonds (green in Figure 10) are formed at different points in time. After formation of three O–H bonds, the O–O bond (orange, also orange in Figure 10) is broken.

seems to be important for the process. Our simulations are rather limited concerning system size and simulation length. Particularly the limited simulation length forbids us to make statements about reactions that were not observed. Also the high density is normally not reached in experiment. Hence,

with our simulations we can only assist the chemical intuition and help to extend the knowledge of a chemist to elementary reaction steps in highly reactive systems.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Density functional theory · highly reactive systems · molecular dynamics · reaction mechanisms

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