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**QUANTUM MOLECULAR DYNAMICS SIMULATION OF HYPERGOLIC REACTIONS
BETWEEN AN ENERGETIC IONIC LIQUID AND NITRIC ACID**

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ABSTRACT

Recently, Energetic Ionic Liquids (EILs) have emerged as potential alternative hypergolic propellants to replace toxic monomethyl hydrazine (MMH). Ionic liquids have no appreciable vapor pressures, are safe to handle and can be tailored to have desired properties. One challenge is to design EILs with short ignition delays. In this paper, we report density functional tight binding molecular dynamics simulations (DFTB-MD) to study initial stages of hypergolic reaction between an EIL and nitric acid. Calculations were performed at various temperatures, and reaction mechanisms were identified. The reaction products, such as H₂O, HNCO and CO₂, predicted by DFTB-MD simulations are in agreement with the recent experiments by AFRL. These simulations predict that the reaction mechanism is very complex and it changes with temperature.

INTRODUCTION

Hypergolic propellants have been used in small to medium range rocket engines since World War II. This category of liquid propellant ignites almost instantaneously when exposed to powerful oxidizers, such as IFRNA. Currently the most widely used hypergolic propellant is MMH. Although monomethyl hydrazine (MMH) has been used for decades, it is highly toxic and carcinogenic. It also has high vapor pressure at room temperature which makes it difficult to handle and transport. In addition, recent environment and health concerns encourage the development of environment friendly fuels. Therefore, one of the major goals of the Air Force, and in general, DoD is to search for hypergolic propellants that can replace MMH without sacrificing its performance. Recently Energetic Ionic Liquids (EIL) have emerged as an attractive alternative due to their potential applications as hypergolic bipropellants¹⁻⁵. Due to their negligible vapor pressure, they are more environment-friendly and safe to handle and transport than the currently used hydrazine based fuels. In addition, EILs are amenable to the modification of their physical properties such as density and melting point via the introduction of different chemical functionalities. For these reasons, EILs are being seriously considered as next generation hypergolic propellants.

The most important aspect of a hypergolic fuel is its ignition delay (ID) time when mixed with an oxidizer, such as IRFNA. The longer the ID is, the larger the combustion chamber must be to avoid pressure spikes that could rupture the engine. So, a short ID is a necessary condition for hypergolic fuel. Therefore, the current challenge is to design a hypergolic fuel which is high-performing, nontoxic, safe to handle and transport, has ID comparable to MMH (~5 ms) and can be used with existing propulsion systems with no or minor modifications. Although EILs have come long way towards meeting these requirements, their ID is still considerably longer than MMH. Therefore, one challenge is to design EILs with short ignition delay. Currently there is no technique to predict ID prior to synthesis of EILs. Very recently, we have developed a preliminary model for ID prediction using a Quantitative Structure Property Relationship (QSPR) and Artificial Neural Network (ANN). Although these predictive models are useful for design purposes, it does not provide fundamental understanding of the reaction mechanism.

In order to obtain a fundamental understanding of these reaction steps, quantum based methods are the methods of choice. The quantum based methods are quite complex, time consuming and often require multi-disciplinary expertise. For example, ab initio quantum chemical calculations when combined with reaction rate theory and kinetics modeling can, in principle, be capable of predicting the ID. However, such a procedure is extremely time consuming (may take years for

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each EIL), and each EIL must be studied on a case by case basis. Therefore, such a method is not practical, but can be useful in understanding some of the fundamental aspects of ignition reactions. Quantum molecular dynamics (MD), when used in conjunction with semi-empirical forcefields, is faster than ab initio calculations, and reveals the dynamics of bond-making and breaking. In addition, such calculations can be done for several hundred of atoms with minimal computer resources, and a realistic nitric acid environment can be set around an EIL molecule for accurate predictions. This is in contrast to high level ab initio methods where calculations are inherently with vapor phase approximations. Although, at present, quantum reactive MD calculations cannot be performed at the millisecond time scale (i.e. the time scale of ID), one can, at least, obtain some insight into the initial stages of hypergolicity. We therefore preferred quantum reactive MD simulation with density functional tight-binding (DFTB) forces over traditional ab initio methods to obtain fundamental understanding of hypergolic reactions. We will refer this technique as DFTB-MD in our following discussion.

In this paper, we first outline the DFTB-MD method. We then perform DFTB-MD simulations at various temperatures, identify the predicted reaction products and reaction pathways at various temperatures.

RESULTS AND DISCUSSION

Computational Method

One of the major advantages of this method is that the forces required for atom movements are computed using a self-consistent charge tight binding method (in the framework of density functional theory) on the fly without using any empirical analytical expressions. Since it is based on quantum formalism, the chemical reactions are naturally taken into account, and no special treatment is required for chemical reactions. Recently, the same technique has been successfully applied to study the dynamics of HMX decomposition in extreme conditions⁶. To our knowledge, this is the first report of applying DFTB-MD to study hypergolicity between an EIL and nitric acid. In the following, we outline the main features of the DFTB method, and we refer to the literature for additional details⁷⁻¹⁰.

- ✓ The DFTB method is based on the second order expansion of the Kohn-Sham energy functional from DFT with respect to charge density fluctuation relative to a reference density.
- ✓ Unlike the traditional tight-binding method, the DFTB calculates the charge transfer between atoms and performs population analysis similar to that done in other sophisticated quantum chemical methods.
- ✓ Like DFT, DFTB uses non-orthogonal atomic orbitals.
- ✓ The repulsive part of the energy functional, which is a sum of inter-atomic two-body potentials, is obtained by fitting with small molecules using DFT data.

MD simulations were performed with constant volume and a fixed number of atoms. Two types of simulations were performed: 1) increase in temperature from 10K to 3000K with time, and 2) at a constant temperature. The increasing temperature simulation was performed in order to examine the sequence of events that happens as the temperature changes rapidly. The time step used for MD simulation was chosen to be 1 fs. At each time step, DFTB forces were calculated, and Velocity Verlet algorithm was used to determine the position of the atoms in the following time step. All simulations were run at least up to 10 ps.

Model Construction

We chose 1-allyl-3methyl imidazolium dicyanamide, an EIL, and pure HNO₃, an oxidizer, to study the hypergolic reactions. In order to study the reactions correctly, it was critical to construct an appropriate and a reasonably realistic model. To accomplish this, we first constructed a simulation box with dimension of 24Å x 12Å x 12Å filled with nitric acid. An appropriate number of

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nitric acid molecules were put into the box so that it approximately reproduced the experimental density of the nitric acid (1.51 gm/cc). The total number of nitric acid molecules therefore considered was 50. Periodic boundary condition was applied so that when an atom left the box during the simulation, another one was inserted in an equivalent position from the opposite direction. The preliminary nitric acid configuration was optimized for 100 optimization steps in DFTB in order to obtain a relaxed configuration. However this resulted in an ordered structure, instead of a disordered liquid structure. To obtain a liquid structure, we gradually heated up the system from 0K to 600K, where the system melted, and then cooled down to room temperature (298.15K). This procedure yielded a disordered liquid structure for nitric acid, as shown in Figure 1.

We then manually inserted one molecule of EIL in the middle of the simulation box by removing three molecules of nitric acid. Such an adjustment kept the density of the system nearly unchanged. The entire configuration, except the atoms in EIL, was further relaxed in order to minimize close contacts. The atoms in EIL were fixed to prevent any bond breaking or forming during the minimization steps. Before the EIL was inserted, the gas phase geometry of the EIL was optimized with DFTB and charges were examined. The charges on the cation and anion were found to be very close to +1 and -1, respectively confirming that the DFTB charge distributions were correct. The EIL containing box filled with nitric acid was taken as starting point of our MD simulations (Figure 2).

It should be noted that IDs for hypergolic reactions with nitric acid are of the order of 10^{-3} s and longer. Reactive MD simulation with such time scale has not been reported to date, and it is impractical to cover such a time scale with standard MD techniques. However, coupling of DFTB with Temperature Accelerated Dynamics (TAD)¹¹ could allow simulation of such a time scale. It should be pointed out that the TAD is not the same as artificially increasing the temperature to enhance the reaction rate, which is used for the reported simulations in this study and is the most widely used technique to study slow chemical processes. The goal of the present investigation, therefore, is not to study the progress of hypergolic reactions over the real time scale, but to get an idea of the reactions and intermediates that might be involved during the initial stages of reaction.

Simulation Results

As mentioned earlier, two different types of simulations were performed: 1) increasing the temperature with time and 2) at constant temperature.

Simulation with Increase in Temperature with Time to 3000K:

In this simulation, the temperature of the system was increased from 10K to 3000K over a time period of 7 ps, and then kept constant for another 3 ps. The objective was to follow the sequence event as the temperature increased.

Figure 3 shows the reactions that occurred during the time of the simulation. Figure 4 shows the snapshots at different times when these reactions occurred. The dicyanamide (DCA) anion picked up two protons and was simultaneously oxidized, then split into HNCO and HNCN. The formation of HNCO occurred at around 7 ps with the current simulation conditions. On the other hand, the methyl group in the side chain was oxidized to $-\text{CH}_2\text{OH}$. On the other side chain, the terminal double bond rearranged (from 3 position to 2 position). The HNCN, which formed from the DCA, attacked at the side chain of the cation. This was followed by a series of reactions (oxidation and bond breaking) leading to acetylene and CO (via HCO). HCO (which is the precursor for CO formation) was formed along with HNCN which appeared to be responsible for rupturing the cation completely. HNCN finally was converted to $\text{H}_2\text{N-CN}$ and remained stable until end of simulation (10 ps). One important observation in this simulation was the formation of HNCO from DCA which was experimentally observed by the AFRL group.² We have not observed any CO_2 and N_2O formation during the length of the simulation. However, there is a

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possibility that CO could further be oxidized to CO₂ at a much longer time scale. In this simulation we did not observe the formation of oxides of nitrogen from the IL, but their formation from nitric acid could not be ruled out since there were many oxidation reactions in the system where one of the oxygens of HNO₃ was donated. In all MD simulations presented here, we have identified and tracked the intermediates and products by visual inspection of the trajectories.

Simulation at 1000K:

Simulation was performed at a constant temperature of 1000K with the same initial condition as before. The DCA anion quickly picked up a proton to form NC-NH-CN. However, anion and protonated DCA did not react during the time-scale of the simulation (10ps). This clearly indicates that the time-scale of reaction is too large compared to that of MD, and reactions could not be observed unless the temperature is artificially increased or the TAD methodology is implemented and used.

Simulation at 2000K:

At 2000K, as observed for 1000K, protonation of DCA occurred. The unsaturated side chain of the cation was oxidized and detached from the imidazolium group. The products formed during the time of simulations were an unsaturated aldehyde and 1-methyl imidazolium ion (Figure 5).

Simulation at 2500K:

Unlike at 1000K and 2000K, many events were observed at 2500K (Figure 6). The anion captured a proton to form NC-NH-CN and then HCH-N-CN. The protonated anion eventually was oxidized to form HNCO and HNCN via a series of rearrangement and decomposition reactions. The final step for HNCO formation happened at 9.98 ps. On the other hand, the methyl side chain of the cation was oxidized to form formaldehyde (H₂C=O) which led to CO *via* HCO formation (at 2.92 ps). The five-membered imidazole compound (remained after the oxidation of the methyl group) underwent a series of reactions, such as oxidation, hydrogen abstraction and ring rupture. The rupture of the C-N bond in the ring occurred *via* reaction with HNCN which formed from the anion. We continued this simulation for 25 ps in order to observe the fate of the five-membered ring. The most important finding was the formation of CO₂ *via* oxidation of the imidazole compound. We also observed some H₂O as byproduct. The important chemical transformations are shown in Figure 7.

Simulation at 3000K:

Reactions observed at 3000K simulation (constant temperature) are shown in Figure 8. Figure 9 shows the important structures formed at different times during the simulation. At 3000K, the DCA anion captured a proton (NC-NH-CN → NC-N-CN_H), and then abstracted a hydrogen from H₂O (formed *via* 2HNO₃ → NO₂ + NO₃ + H₂O) to form a short-lived HNC-N-CN_H species which immediately formed HNC and HNCN. HNC finally was oxidized to NO and CO *via* a series of reactions including HNCO. In fact, HNCO formed at 3.56 ps, lived until 5.52 ps and then was converted to NCO. NO and CO formation occurred at 6.74 ps at this temperature. One other hand, allyl side chain of the cation lost two successive hydrogens to form a triple bond. The methyl side chain was oxidized to formaldehyde which eventually produced CO (H₂C=O → HCO → CO). Formation of CO from cation occurred much faster (0.92 ps) than that from the anion. The cyclic part, present after oxidation of the methyl side chain, underwent several reactions: a) ring opening, b) ring expansion to form a pyridine-like structure, c) rupture of the pyridine-like structure *via* oxidation and d) finally the formation of CO, NO and HCN. A CN fragment, generated from the pyridine-like structure, reacted with HNCN (formed from the anion) to form HNC-C-CN which eventually was converted to HNCO *via* oxidation at 9.72 ps. The major finding of this simulation is the mechanism for formation of HNCO, NO and CO. HNCO and CO formed from both anion and cation of the IL. Also, like at 2500K, we observed H₂O formation. One of the most interesting aspects of these simulations is that the mechanisms of HNCO, CO and NO

formation were different at different temperatures. This gives some indication that the hypergolic reaction of the EIL could be more complex than thought before.

SUMMARY AND CONCLUSIONS

This paper reports, for the first time, DFTB-MD simulations to understand the initial stages of hypergolic reactions between an EIL and nitric acid. In these simulations, an EIL molecule was placed in a bath of nitric acid. The simulations were performed at various temperatures (such as 1000K, 2000K, 2500K and 3000K), and the products and reactions were identified. The products identified were HNCO, CO, NO, NO₂, CO₂ and H₂O. It should be noted that HNCO and CO₂ were observed by the AFRL group in their experimental study.² However, we did not observe N₂O (as observed by experiments) during the timescale of the simulations. We anticipate that N₂O will form at much later stages in the process. DFTB-MD simulations show the reaction between the EIL and nitric acid to be very complex, and that the mechanism appears to be significantly different at different temperatures.

ACKNOWLEDGMENTS

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FIGURES

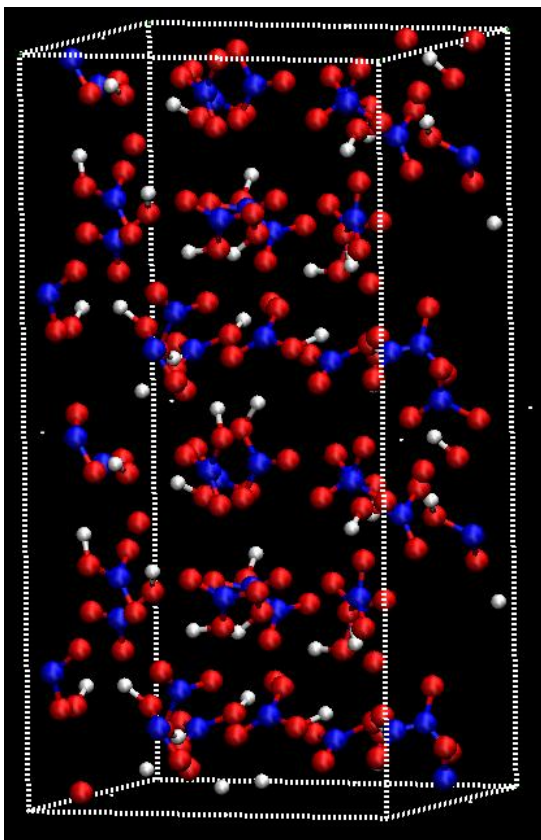


Figure 1: Liquid Structure of Nitric Acid

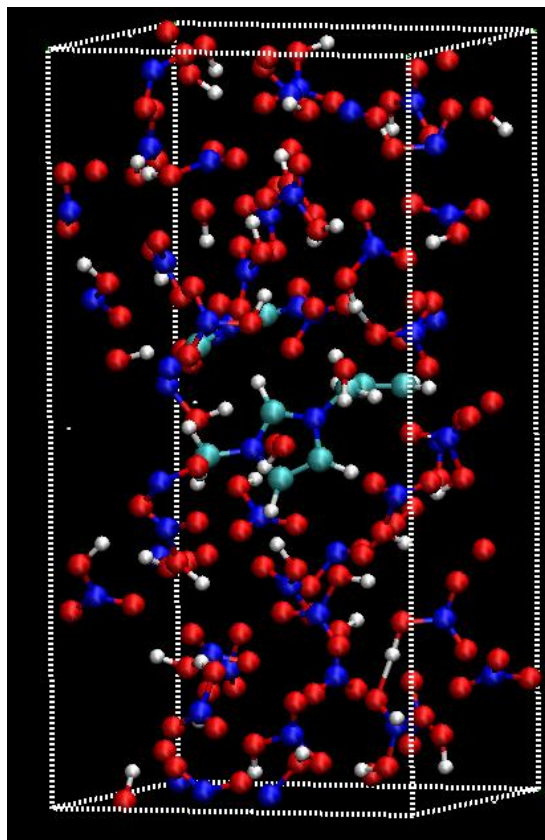


Figure 2: 1-allyl 3methyl dicyanamide EIL in HNO₃. This is the Starting Configuration for All Simulations.

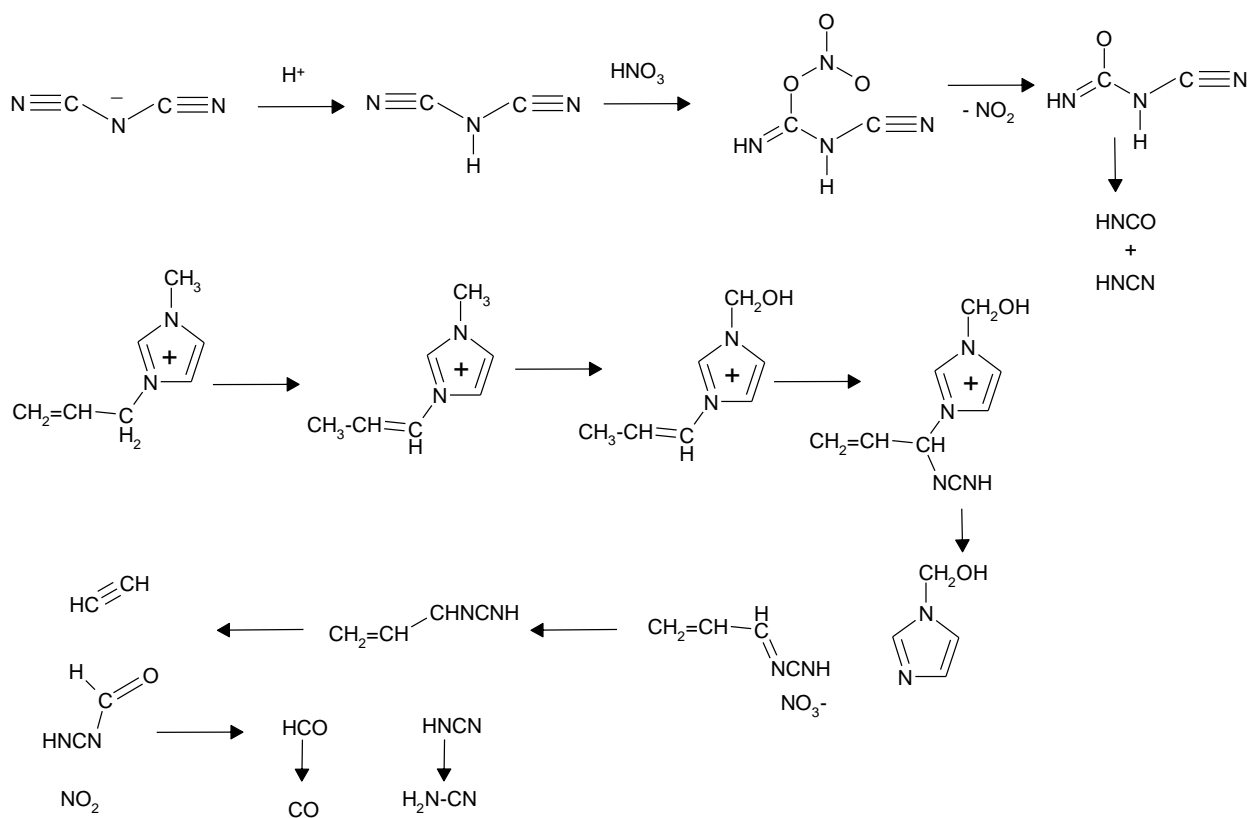
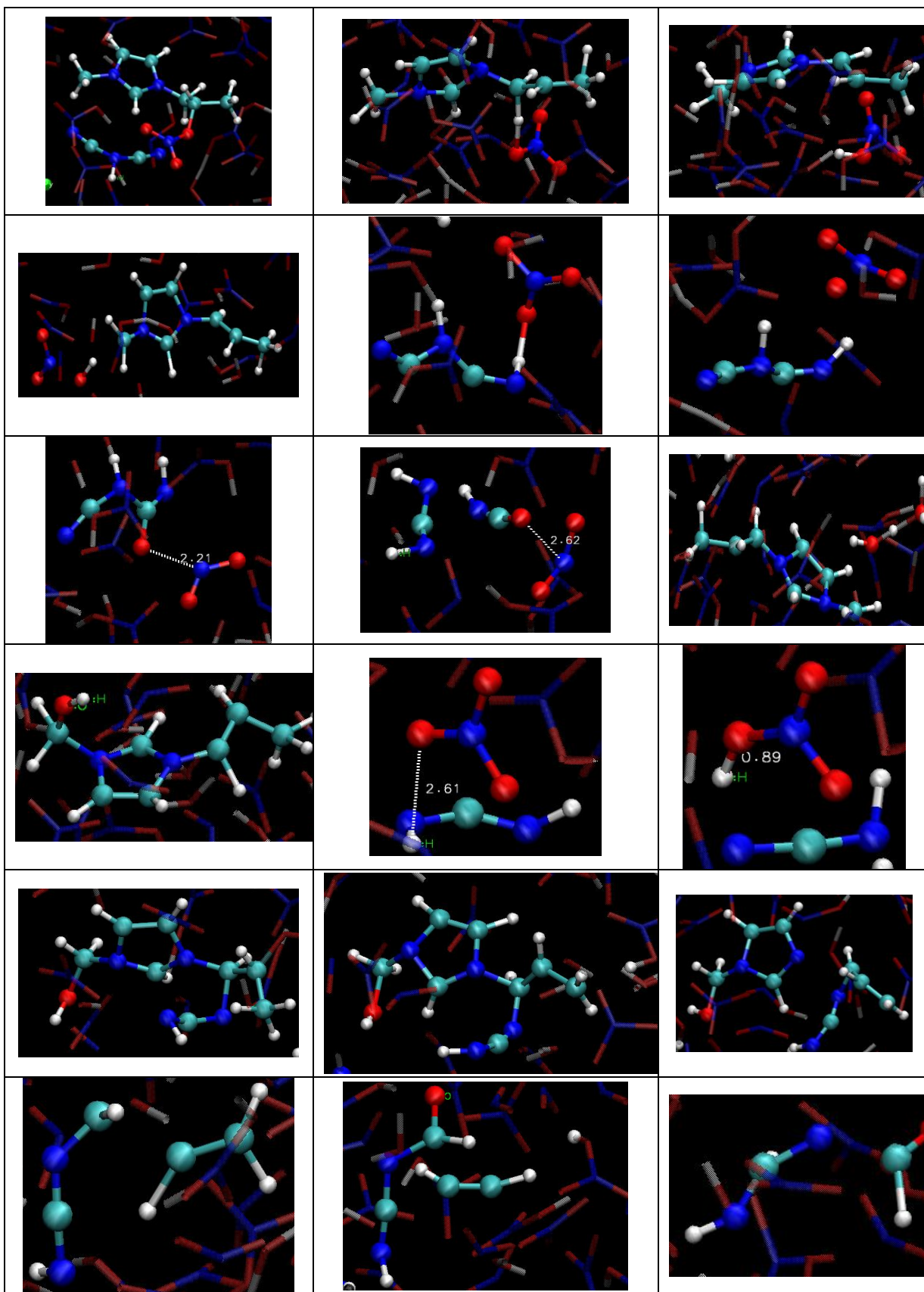


Figure 3: Reactions Observed During Simulations with Gradual Increase in Temperature to 3000K. Intermediates Shown Above are Actually Observed During the Simulation.



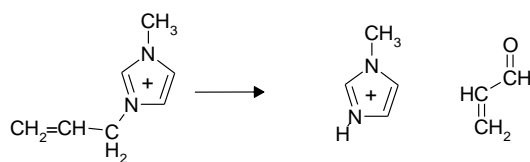
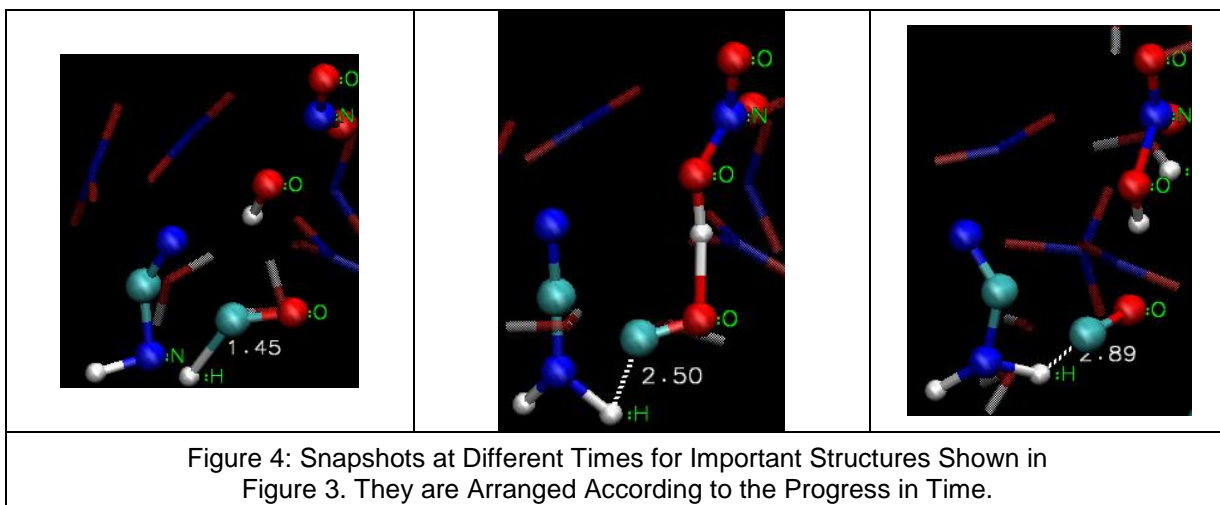


Figure 5: Oxidation Reaction Occurred at 2000K. Intermediates Shown Above are Actually Observed During the Simulation.

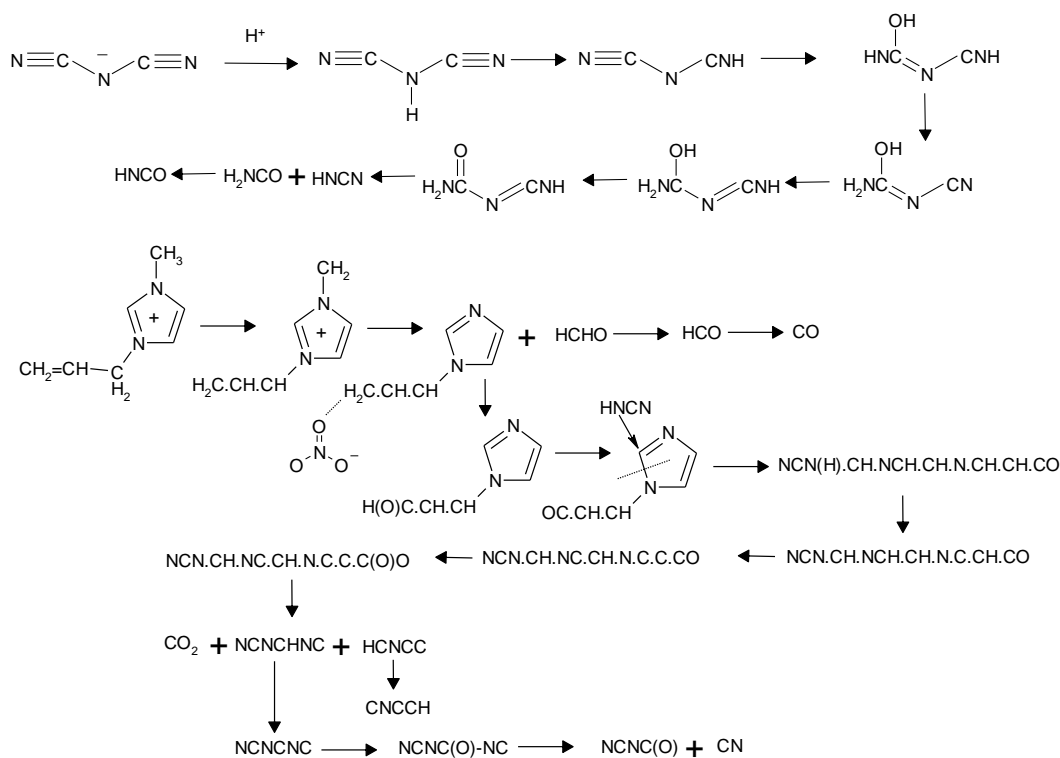
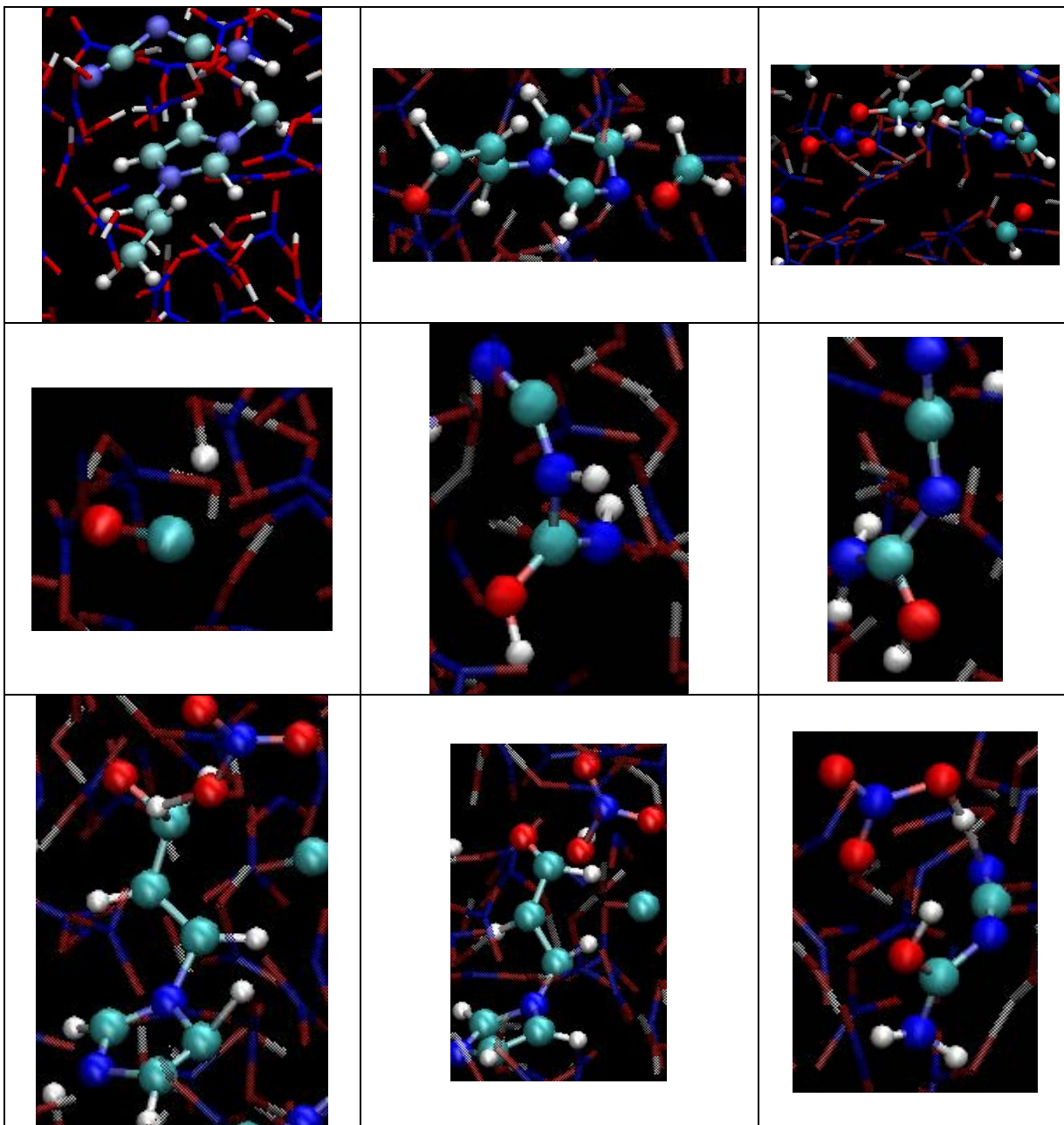
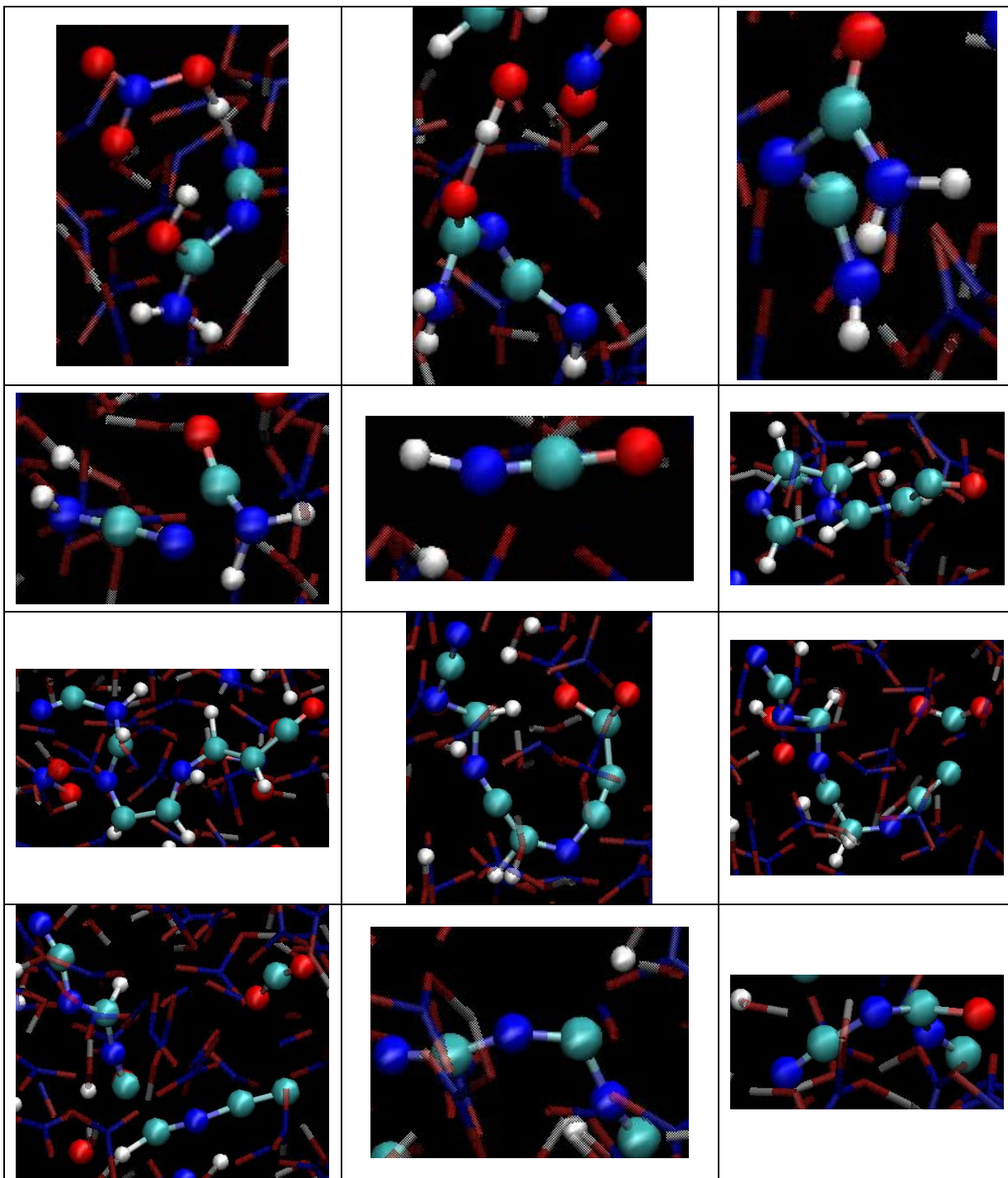
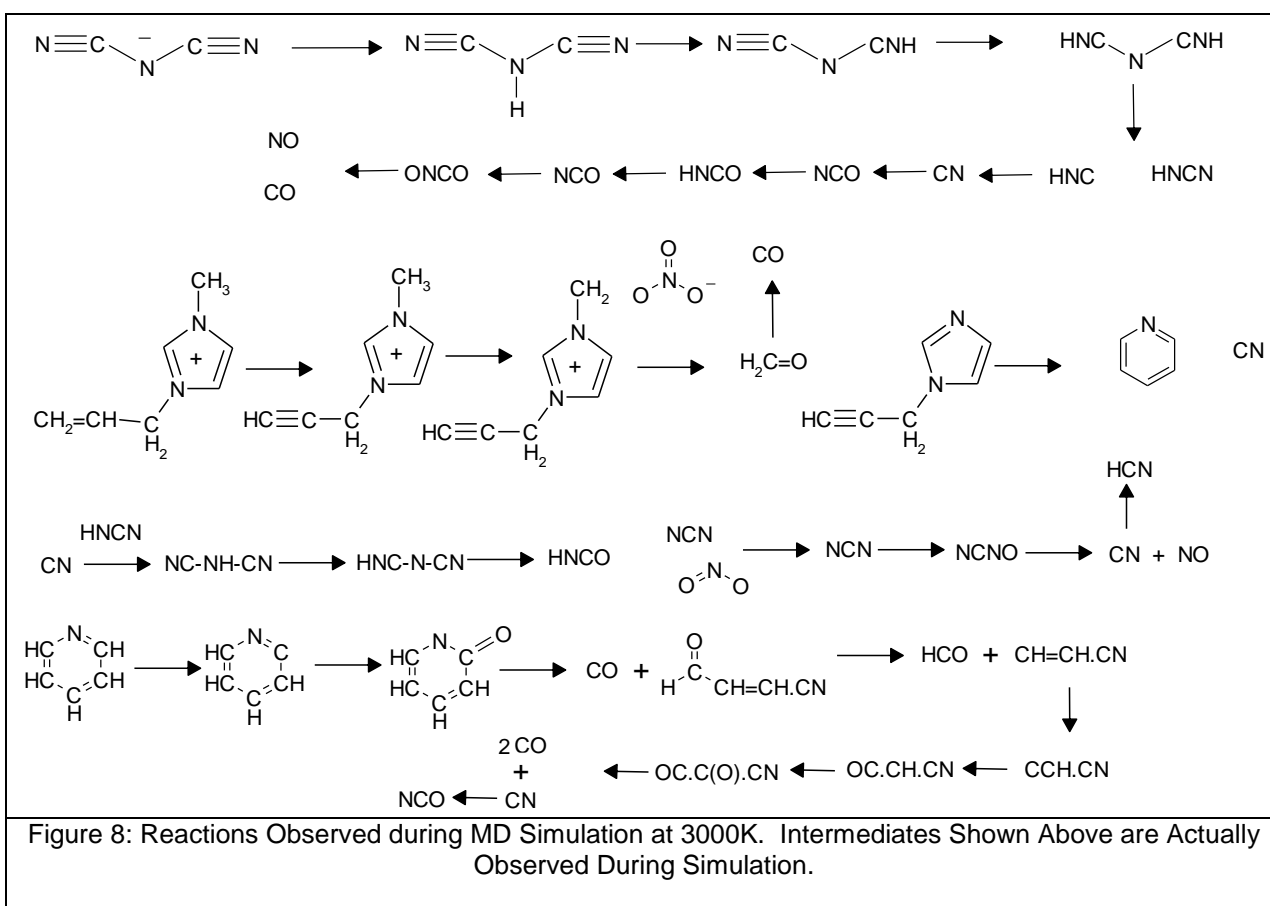
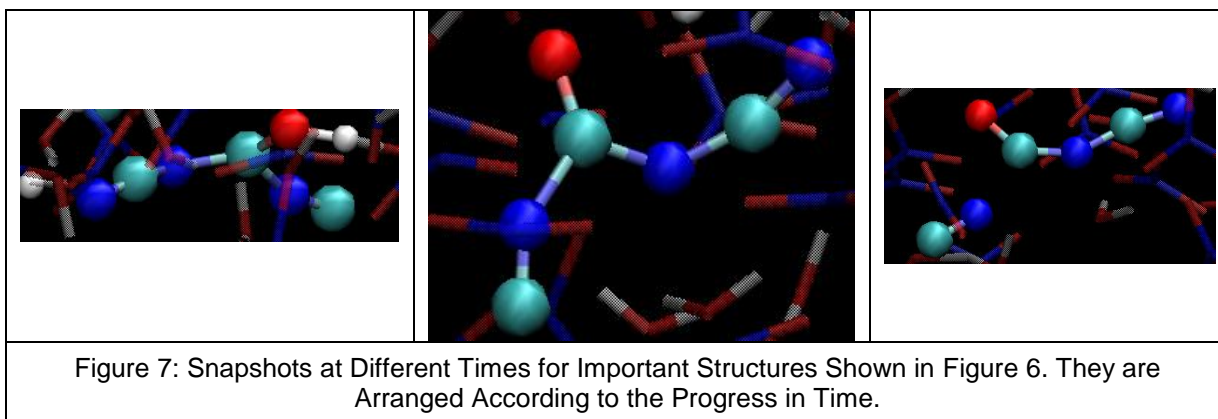


Figure 6: Reactions Observed During MD Simulation at 2500K. Intermediates Shown Above are Actually Observed During the Simulation.







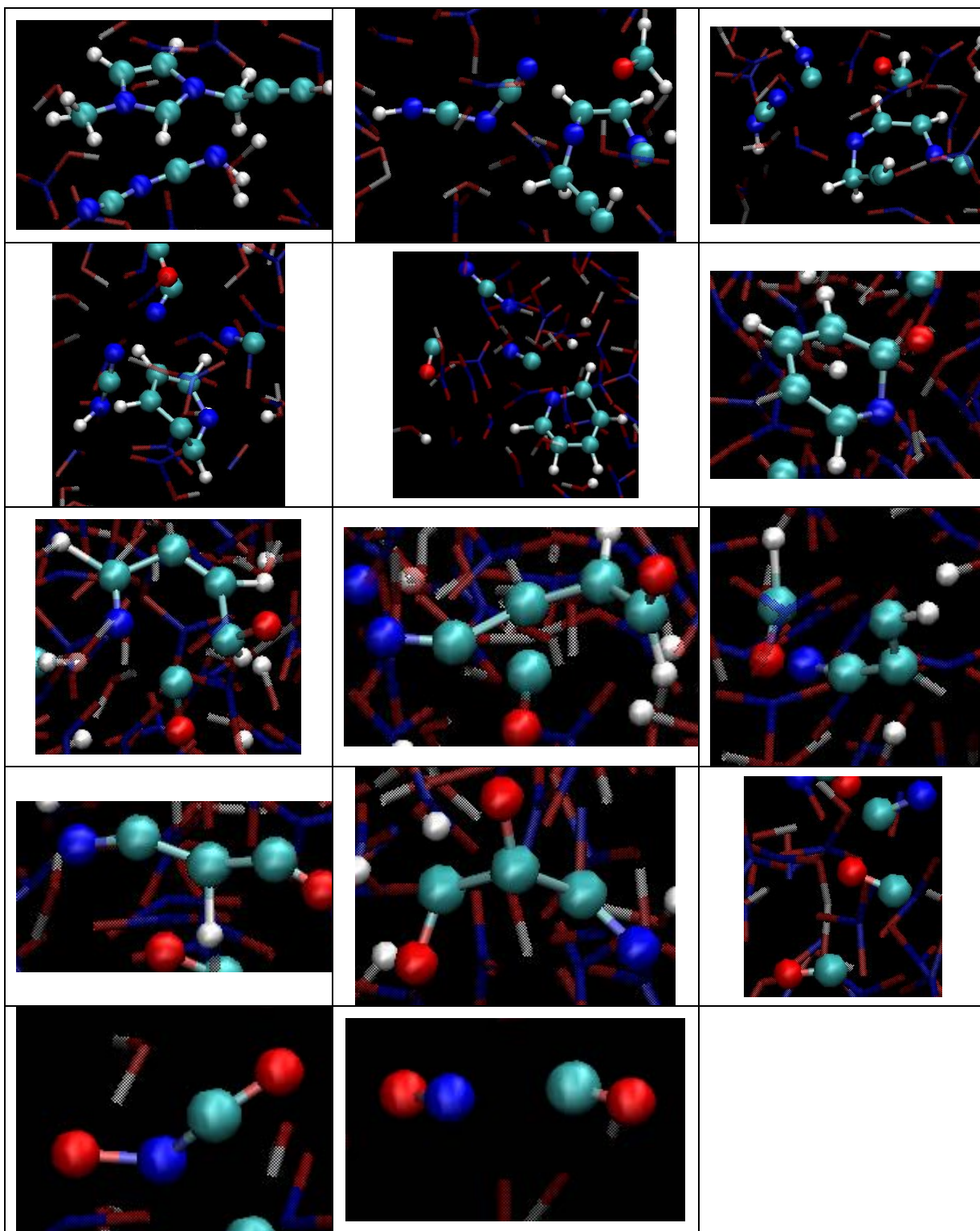


Figure 9: Snapshots at Different Times for Selected Important Structures Shown in Figure 8. They are Arranged According to the Progress in Time.