

Mechanisms and Kinetics of Thermal Decomposition of CL-20

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This summary is abstracted from the paper, “An *ab initio* Molecular Dynamics Study on the Initial Chemical Events in Nitramines: Thermal Decomposition of CL-20,” which is accepted for publication in the *Journal of Physical Chemistry*, ID: jp-2008-04765m and provides the basis for our AICHE presentation.

In contrast to past studies of thermal decomposition mechanisms of explosives designed to determine the detailed chemical pathways by which these large organic molecules are transformed into small reaction products (N₂, NO, N₂O, HCN, CO, CO₂, H₂O, etc.)—crucial to predicting long-term stability for storage; sensitivity to heat and mechanical impact; and risk assessment associated with their usage, the purposes of this study were to investigate the initial chain of chemical events during CL-20 decomposition of isolated and condensed phases and, additionally, to analyze the nature, energetic, and kinetic patterns of the primary and secondary products. To improve atomistic understanding of the thermal decomposition of solid phase CL-20, (a high-energy nitramine explosive possessing R₂N-NO₂ functional groups) we performed a series of *ab initio* molecular dynamics simulations, finding that during unimolecular decomposition, unlike other nitramines, CL-20 has only one distinct initial reaction channel—homolysis of the N-NO₂ bond. No HONO elimination reaction was observed during unimolecular decomposition; the ring breaking reaction was followed by NO₂ fission.

Therefore, in spite of limited sampling, we propose a scheme of unimolecular decomposition of CL-20. The averaged product population over all trajectories was estimated at 4 HCN, 2-4 NO₂, 2-4 NO, 1 CO, and 1 OH molecule per one CL-20 molecule. Simulations provided a detailed description of the chemical processes in the initial stages of thermal decomposition of condensed CL-20, allowing elucidation of key features of such processes as composition of primary reaction products, reaction timing, and Arrhenius behavior of the system. The primary reactions leading to NO₂, NO, N₂O and N₂ occur at very early stages. We also estimated potential activation barriers for the formation of NO₂, which essentially determines overall decomposition kinetics and effective rate constants for NO₂ and N₂. The calculated solid phase decomposition pathways correlate with available condensed phase experimental data.

Approach: The elementary reactions involved in the complicated decomposition process were obtained directly from the MD trajectories. First, a set of trajectories was collected by simulating an isolated CL-20 molecule at various temperatures. In addition to unimolecular decomposition, significant effort was also spent on analysis of condensed phase reactions. Consequently, the unimolecular decomposition process was analyzed only *qualitatively*. In the second part of the research, we produced an overview of atomistic mechanisms of decomposition of crystalline CL-20 and estimated the rate constants of the primary and secondary reactions under constant high temperature conditions.

For the first time, a series of *ab initio* molecular dynamics simulations were performed to shed light on the chain of chemical events of thermal decomposition of isolated and crystalline CL-20, revealing a qualitative picture of reaction pathways of unimolecular decomposition of CL-20. High

temperature simulations perfectly agree in prediction of key reactions and leading products over a broad temperature range on the ten picoseconds scale. This process was found to proceed via formation of cyclic intermediates. The averaged product population was also estimated.

The activation barrier for the formation of NO_2 , which essentially determines the overall decomposition kinetics, was estimated, and the effective rate constants for NO_2 and N_2 was evaluated. Unfortunately, the short time scale accessible to the first principle simulations did not allow estimation of characteristic reaction time and product lifetime.

Several important differences were found from the earlier empirical (FeaxFF) and tight-binding simulations of other cyclic nitramines. These include dramatic differences in concentration and reaction rates for water, carbon monoxide and carbon dioxide. Therefore, it is not clear whether differences are due to the distinct chemistry of monocyclic (RDX, HMX) and polycyclic (CL-20) nitramines, to the nature of underlying electronic-structure methods, or even to the simulation setup, e.g., type of dynamics, choice of thermostat, etc.

Overall, doubling the system size of the simulation box did not introduce significant differences as to facilitating exploration of the reaction processes. Therefore, a one unit cell was enough to observe the most important features of the process and to make semi-quantitative estimations of thermodynamic and kinetic parameters. However, due to the larger temperature fluctuations in the smaller system, it appears to have slightly faster kinetics and larger fluctuations in product concentrations. Thus, a larger system size is desired for obtaining a more precise product time evolution series and higher accuracy.

Isolated System: For calculation of the gas-phase molecule, a 18 Å cubic supercell was used with a cell length chosen to be large enough to prevent interactions between periodic images. The effect of the unit cell length was checked by expanding the box size to approximately 20 Å. Only a minor variation in the total energy was found. The geometry of the system was minimized and subsequently equilibrated at the NVT ensemble. After equilibration, five independent production runs with target temperatures of 1000, 1500, 2000, 2500 and 3000K were initiated. To improve observed statistics, each simulation was repeated at least one more time, starting from a different configuration. The length of simulations varied from 5 to 10ps and actual temperature fluctuations were within 50-150 K from those desired.

Crystal Phase: In order to obtain better statistical sampling and test system size dependence, simulations were performed with larger supercells (1×1×2 unit cells, eight CL-20 molecules, 288 atoms). The system was constructed by merging two equilibrated unit cells along the c axis (smallest axis). After a 1ps quick re-equilibration, production runs were initiated at 2000 and 3000K. The lengths of simulations were 5.1 (aborted due to hardware failure) and 15.4ps respectively; the actual temperatures were 1947 and 2882 K, respectively.

It was observed that homolysis of the N– NO_2 bond occurs on the 0.1-0.5 ps scale, depending on temperature. As expected, the higher the temperature, the faster the reaction proceeds. No clear temperature dependence of the number of broken N– NO_2 bonds was found. Seven of ten trajectories (including the most and least extreme) resulted in fission of all six nitrogroups, which is in perfect agreement with the mass spectral pattern, where peaks corresponding to elimination of 3-6 NO_2 groups were observed. No distinct differences between axial and equatorial nitrogroups were observed, probably due to the fact that, under such extreme conditions, the activation barrier difference of several kcal/mol⁴⁴ becomes negligible. It is quite probable that, due to the limited statistical sampling, this list is not exhaustive of all possible geometrical variations. However, seven out of ten trajectories resulted in 12-atomic intermediates. This species oscillates around planar geometry and is stabilized by adoption

of an aromatic structure with typical C-N bond lengths, ranging from 1.2 to 1.45 Å, and having a lifetime of approximately 0.5ps at 3000 K and quickly increasing to 9ps at 1500 K.

Three major distinctive channels were found for subsequent decomposition of CL-20 intermediates. These secondary reactions include: a) fragmentation, b) oxidation by a NO₂ radical, and c) hydrogen abstraction by a NO₂ radical. Fragmentation of the intermediate results in stepwise breaking into HCN molecules. Oxidation by NO₂* yields N-methylenformamide derivatives and NO (Figure 1), leading to further decomposition. Methylenformamide derivatives undergo fast decomposition, eliminating 1-2 HCN molecules (depending on molecular length) and yielding simplest methylenformamide carbenes, and leading to final the CN-COH molecule degradation. The third pathway represents hydrogen abstraction by NO₂, resulting in HONO molecules. This is an interesting variation of HONO molecular formation, formed during the later stages of the reaction ($\tau > 2$ ps) by interaction of the NO₂ free radical and the intermediate. Based on our knowledge, this reaction has not before been described in nitramines, neither experimentally nor theoretically. This finding is in contrast to the suggested concerted *intramolecular* mechanism of HONO formation in RDX/HMX,^{20,21,45} where departing NO₂ groups capture hydrogen radical. Our results strongly favor the stepwise red-ox *intermolecular* process. Evidence was also found relating to the possibility of formation of an NO₃. From ten simulations, NO₃ occurred only once, at T = 1500K. Two NO₂ radicals combined form NO and NO₃. For a short time (< 1ps) they formed a complex very similar to the ion pair, nitrozonium nitrate (NO⁺NO₃⁻).⁴⁹ After that step the system recombined to the original NO₂ radicals.

Overall, total decomposition (starting from CL-20) into two- or tri-atomic molecules occurred within 4.5-5ps at 3000K. A similar process took approximately twice as long at 2000-2500K. The present timescale was not sufficient to observe total decomposition at 1500 and 1000K. For the latter, a much longer simulation (perhaps in the order of 0.1ns – 1.0ns) is needed to reveal full decomposition of CL-20.

Therefore, in spite of the fact that CPMD simulations of isolated CL-20 presented in this section provide a mostly *qualitative* picture, high temperature simulations on a ten picoseconds scale perfectly agree as to primary reactions and leading products over a broad temperature range. The averaged product population over all trajectories was estimated to yield 4 HCN, 2-4 NO₂, 2-4 NO, and approximately one CO, and one OH molecule per one CL-20 molecule. Due to the lack of CL-20 gas phase experiments, those population numbers cannot be compared with observed ones.

Decomposition of CL-20 in the condensed-phase: There is clear enhancement of the decomposition process with temperature increase. Therefore, starting with the fastest reaction, the kinetics of the predominant intermediates and reaction products can be analyzed in detail, despite available limited computational facilities allowing simulation of only the initial steps of decomposition.

The eight picosecond time scale was almost sufficient to reach product equilibrium concentration at T=3000 K. All nitrogroups quickly decayed within the first 800fs. At the same time, the number of NO₂ radicals proportionally increased, reaching a maximum of 13 molecules at t=400fs. By the time ~2.5 ps was reached, practically the entire concentration of NO₂* was consumed. Similarly, nitric oxide accumulated to ~1.2 ps, with a maximum concentration of 16 molecules per unit cell, after which it slowly reacted into N₂, N₂O, and NOH, reaching equilibrium at a concentration of 5-6 molecules per unit cell by the end of the simulation. It should be noted, that the equilibrium established here (and for all species later on) is dynamic, i.e. previously formed molecules react and undergo rearrangement, and new species are formed—maintaining approximately constant concentration.

The other experimentally determined ratios are 3.3, 1.2 and 0.82 for CO₂, CO and N₂O, respectively, with calculated values amounting to 1.25, 1.0 and 1.0 respectively. Significant deviation

in the concentration of CO₂ can be attributed to the short time scale and small system size accessible to the AIMD simulation. Indeed, carbon dioxide is a product of the latter stage of the reaction. The length of simulation needed to be at least an order of magnitude longer to observe the steady state formation of CO₂, as well as to detect the CO conversion reaction (CO + H₂O = CO₂ + H₂). The concentration of CO₂ and a few other important products did not establish a well behaved tendency (especially for low temperature simulations) and were found in significantly smaller amounts than the species described above. By the end of the simulation, the reaction mixture included three molecules of H₂O and CO; two of OH radical; and one of HCN, CO₂, NH₃, HCNO, CN, NOH, and CNC(O)H.

Decrease of simulation temperature to 2500 K slowed the whole reaction process. On one hand, the decaying of nitrogroups was only slightly affected; just one picosecond was needed to complete this process. On the other hand, as much as twice the time (about 4 ps) was needed for formed NO₂ to react, starting from a peak concentration of 14 molecules per unit cell to equilibrium. Further, the decomposition reaction did not reach equilibrium concentrations of both NO and N₂. The observed values were 8 and 15 molecules, respectively. Assuming similar kinetics and C_∞ for molecular nitrogen, the estimated time needed to reach steady stage concentration was found to be ~20 ps, and k=0.3 ps⁻¹. Concentrations of other molecules were found as follows: H₂O, OH radical, and CO₂ – 3; HONO, HCN, and CO – 2.

Further decrease of temperature leads to more dramatic differences in the reaction process. Significant prolongation of the lifetimes for both NO₂ and NO were immediately observed. Concentration of NO₂ at approximately 10 molecules per unit cell was maintained for an additional 3ps. Decay of the NO concentration was barely noticeable, but was still higher than that of N₂. Formation of molecular nitrogen was expected to be delayed for 4.5 ps. The resulting concentrations at t=10.5 ps were NO – 12, N – 11, N₂O, CO₂ – 4, H₂O, CO, OH radical – 2, very far from the values expected at the equilibrium stage. Finally, our least extreme simulation, at T = 1500 K was barely long enough to observe full fission of the nitrogroups. Consequently, the concentration of NO does not reach its maxima. Decrease of temperature also stabilized the concentration of N₂O. Overall, all mentioned approaches provide *qualitatively the same* picture of thermal decomposition for the whole class of cyclic nitramine high-energetic materials. Numbers from larger system size are in better agreement with experimental data than ones derived from the smaller system, which means that the larger simulation system is needed to obtain trustworthy concentration values.

Limited computational resources forced the abortion of the other large simulation at T=2000 at not longer than 5 ps. Compared to the one unit cell run, the large simulation exhibited similar behavior, but slightly slower kinetics. For example, NO₂ fission required 3.5-4 ps to proceed. Produced NO₂ reached its maximum concentration of 16 molecules per unit cell at about 2 ps. Both NO and NO₂ temporarily stabilized at the same concentration, ~10 molecules/unit cell, but only after 4 ps of simulation.

Overall, our simulations revealed the systematic behavior of the entire decomposition process in a wide temperature range of 1500-3000 K. Correspondence between the low temperature experiments and high temperature simulations suggest a unified reaction mechanism for both temperature regimes. A careful analysis of the trajectories indicates complex multimolecular and multichannel processes.

Despite such complexity there are several important differences between the studied phenomena and unimolecular reactions that can be identified. Due to higher density and crystal packing, departing nitrogroups “bombard” neighboring molecules, causing a higher oxidizing and conversion rate, in turn, leading to numerous branching reactions where no distinct intermediate was formed. Another difference relates to the concentrations of N₂O and N₂ forming during the decomposition process. In contrast to the unimolecular process, N₂ makes up the prevalent reaction product in solid phase CL-20.

This difference originates in the fact that rapid branching produces a large number of chain molecules containing the NNO pattern. These molecules formed either directly from original nitrogroups of CL-20 or from simpler compounds (e.g. $R-[N=C=N]^{\bullet}$ and NO). Resulting species with NNO motif are not stable and dissociate yielding N_2O . Finally, the nitrous oxide oxidizes various compounds, producing molecular nitrogen. Unfortunately, it was not possible to identify several distinct reaction channels due to the branching and great number of secondary and other types of reactions.

Finally, all condensed phase simulations have been discussed in terms of the thermal decomposition process. However, similar conditions were also achieved during the steady detonation (Chaman-Jouget) state or Zeldovich-von Neumann detonation. Therefore, the above discussion is useful in describing the detonation process. For detonation, formation of condensed carbon (carbon clustering) is a very important process. No carbon clustering was observed in the present work.

Reaction kinetics: Several experimental studies suggest the predominant role of homolysis of $N-NO_2$ in the first stages of decomposition. It was shown that NO_2 fission reaction is rate limiting and determines kinetics of crystal decomposition. Our calculated time evolution profiles for this reaction mostly follow exponential decay—fitting first order kinetics. However, several curves have a sigmoid shape, implying first order kinetics with autocatalysis. Experimental data suggest that either case could be possible, depending on the decomposition stage. It is not clear whether the origin of the sigmoid shape originates from the simulation artifacts. However, no evidence of autocatalysis has been found at this stage.

This process exhibits typical Arrhenius behavior, allowing estimation of the activation barrier of CL-20 crystal decomposition. According to the linear fit, estimated values of E_a and A are 137 ± 24 kJ/mole and 2.6×10^9 , respectively. Corresponding experimentally determined values varied from 150 to 200 kJ/mol and $\sim 10^{13} - \sim 10^{17}$, depending on experimental setup. Our simulations supported the lower values of the activation barrier. However, statistical uncertainty is quite high. The calculated value of the exponential prefactor A , is at least four orders of magnitude lower than the experimental ones. This discrepancy originates from the number of approximations on the simulation setup. All calculations were performed at NVT ensemble, keeping the volume and number of particles of the system constant. In reality, however, the system expands and undergoes phase transitions during heating. Evolving gaseous products contribute to the mass transport between the sample and environment. Obviously, confined gases like NO_2 , NO, and N_2 significantly affect the entropy of the system and, consequently, the value of A .

Our simulations provide a detailed description of the chemical processes in the initial stages of thermal decomposition of condensed CL-20, allowing elucidation of key features of such processes such as: composition of primary reaction products, reaction timing, and Arrhenius behavior of the system. They clearly indicate that the primary reactions leading to NO_2 , NO, N_2O and N_2 occur at very early stages.