Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Early Thermal Decay of Energetic Hydrogen- and Nitro-Free Furoxan Compounds: The Case of DNTF and BTF

Shuangfei Zhu,[a] Wei Yang,[b] Qiang Gan*[a], Nianshou Cheng [a] and Changgen Feng [a]

[a]. State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China.
[b]. School of Materials Science&Engineering, Beijing Institute of Technology, Beijing 100081, China.
* E-mail: ganqiang@bit.edu.cn

Figure S1 shows the number of DNTF and BTF molecule during the simulation times of 20 ps under the thermal decomposition at 1000 K. From Figure S1, DNTF begin to decompose at about 5 ps, and the number changed to be 0 at about 12 ps; BTF begin to decompose at about 3 ps, and the number changed to be 0 at about 10 ps. Although at the end of the simulation, the numbers of DNTF and BTF are both 0, they do not seem to be completely decomposed, and most of the molecules simply undergo bond breakage.

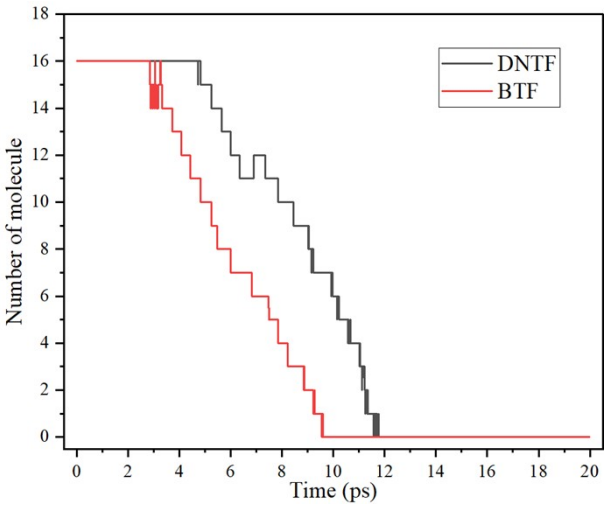

Figure S1. The number of DNTF and BTF molecules under the constant temperature heating at 1000 K

The decomposition reactions of each DNTF molecule were shown in Figure S2. As is seen, the N-O bond of all DNTF molecules were broken, but only 4 molecules decomposed to form two molecular fragments. The reaction **R1** and **R4** (Figure 4) were found during the decomposition of DNTF at 1000 K. It could be concluded that the reaction **R1** dominated the decomposition of DNTF at 1000 K during the simulation. The energy barrier of **R1** is 42.8 kcal/mol of DFTB method (Figure 2), 47.2 kcal/mol of B3LYP/6-311+G(d,p) method (Figure 2) and 25.7 kcal/mol of DLPNO-CCSD(T)[1], which may cause the cleavage of this bond during the MD simulation.

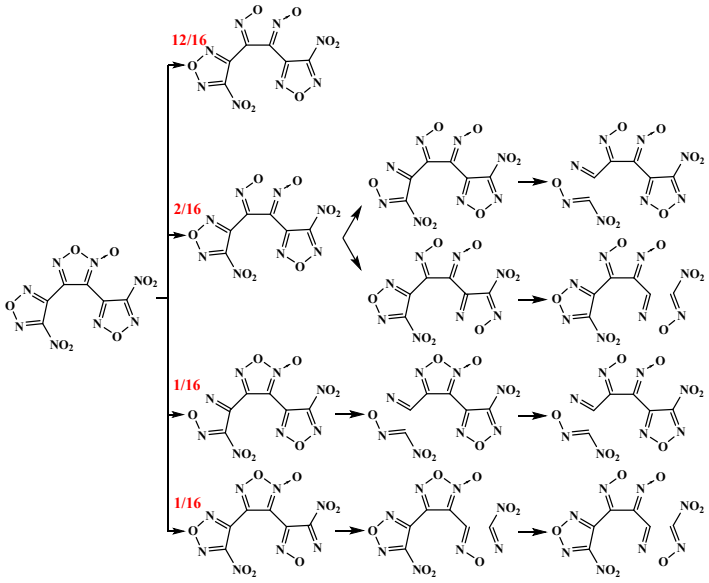

Figure S2. The decomposition behaviour of each BTF molecules under different heating condition. The red number represents the number of molecules.

Figure S3 shows the decomposition reactions of BTF during the simulation at 1000 K. According to the visualization analysis, only this one initial reaction (reaction **a** of Figure 13) was found in the decomposition of BTF at 1000 K. The energy barrier of N(O)-O bond cleavage is 28.3 kcal/mol of DFTB method (Figure 2) or 19.4 kcal/mol of B3LYP/6-311+G(d,p) method (Figure 2). The low barrier of this channel makes BTF sensitive to thermal loading.

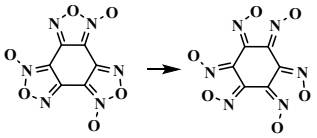

Figure S3. The decomposition behaviour of BTF molecules under different heating condition.

From the above analysis, we can conclude that most DNTF and BTF molecules undergo N(O)-O bond cleavage during the decomposition at 1000 K. At 1000 K, BTF is easier to decompose than DNTF from the decomposition time point of view, which is consistent with the fact of that BTF is more sensitive than DNTF (the drop height of 50% explosion probability (H_{50}) of BTF and DNTF is 21 cm^2 and 31 cm^3, respectively).

The conservation of energy was tested by changing the time steps (0.01 fs, 0.05 fs, 0.1 fs and 0.2 fs) for BTF and DNTF at 3000 K, shown in Figure S2 and S2. Results showed that the total energy of the BTF and DNTF is almost the same with different time steps. Therefore, it can be concluded that the total energy is conserved when the simulation is executed with the timestep of 0.01, 0.05, 0.1 and 0.2 fs.

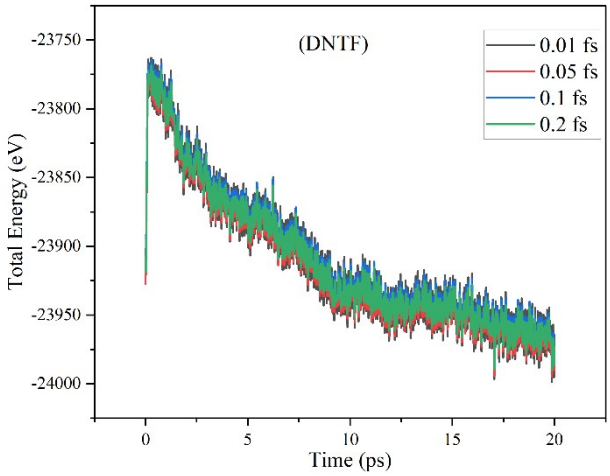

Figure S2. Time evaluation of total energy of DNTF with different timesteps at 3000 K

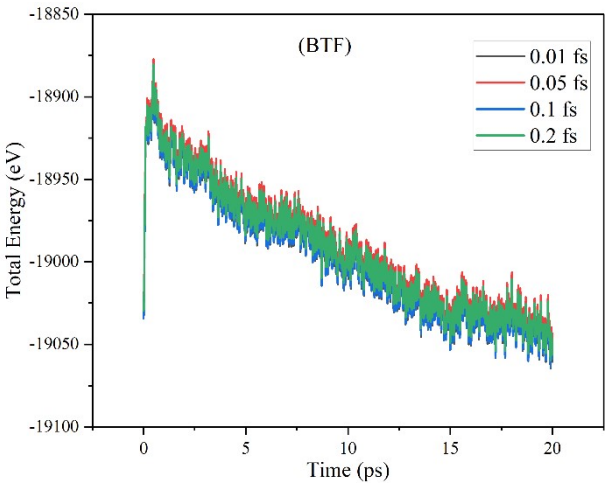

Figure S3. Time evaluation of total energy of BTF with different timesteps at 3000 K

Reference

[1] Zhu, S.; Yang, W.; Gan, Q.; Feng, C. Initial Steps and Thermochemistry of Unimolecular Decomposition of Oxadiazole Energetic Materials: Quantum Chemistry Modeling[J]. J. Phys. Chem. A, 2021, 125, 36, 7929–7939.

[2] Zhang, H.; Guo, C.; Wang, X.; Xu, J.; He, X.; Liu, Y.; Liu, X.; Huang, H.; Sun, J. Five Energetic Cocrystals of BTF by Intermolecular Hydrogen Bond and π-Stacking Interactions. Cryst. Growth Des. 2013, 13, 679-687.

[3] Tsyshevsky, R.; Pagoria, P.; Zhang, M.; Racoveanu, A.; DeHope, A.; Parrish, D.; Kuklja, M. M. Searching for Low-Sensitivity Cast-Melt High-Energy-Density Materials: Synthesis, Characterization, and Decomposition Kinetics of 3,4-Bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole-2-oxide. The Journal of Physical Chemistry C 2015, 119, 3509-3521.